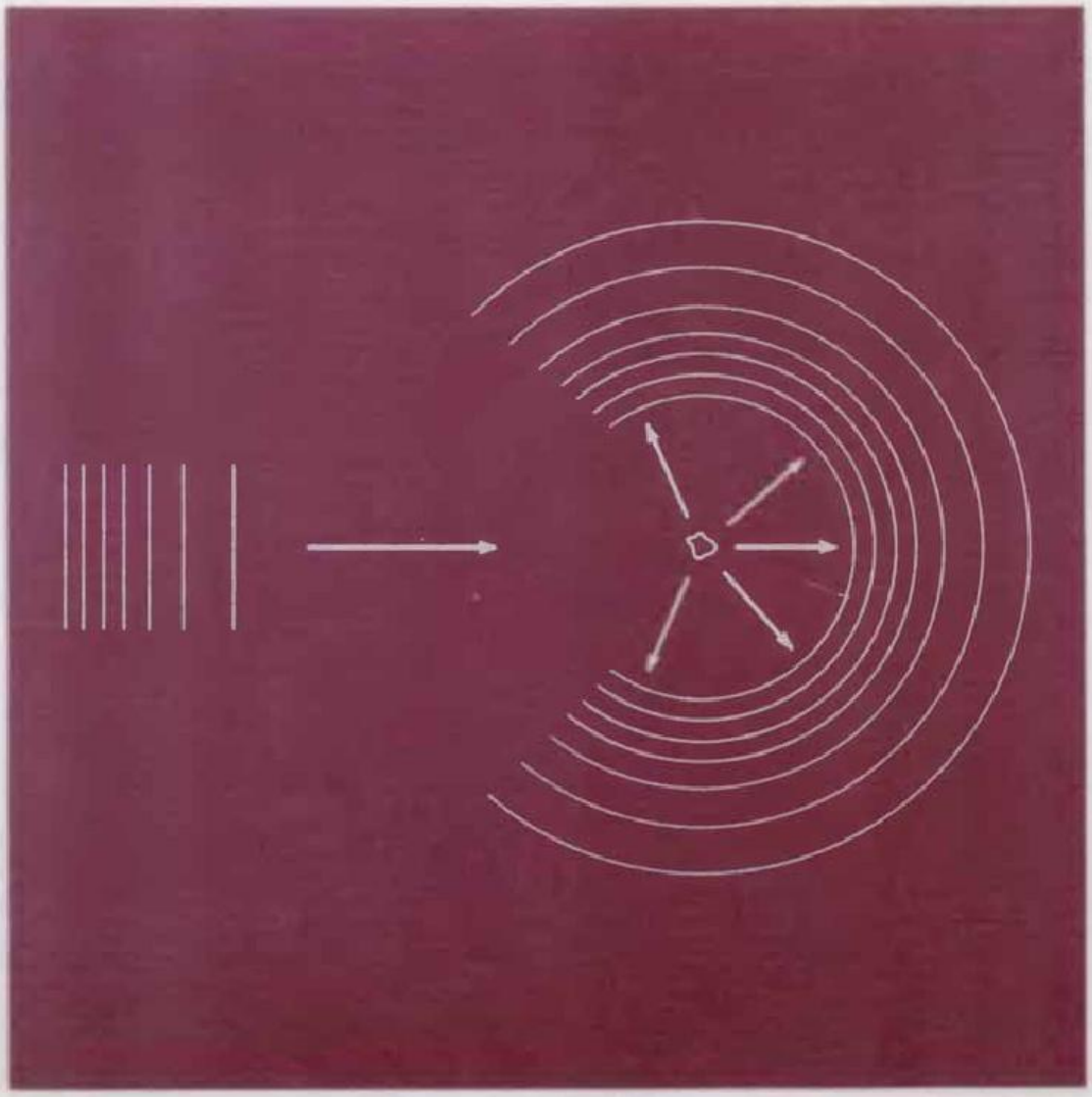
QUANTUM MECHANICS

SECOND EDITION

EUGEN MERZBACHER



Wiley International Edition

QUANTUM MECHANICS

SECOND EDITION

EUGEN MERZBACHER
University of North Carolina

Scanned by terminator

John Wiley & Sons, Inc.,
New York • London • Sydney • Toronto
Toppan Company, Ltd.,
Tokyo, Japan

Contents

1. *Introduction to Quantum Mechanics* 1
2. *Wave Packets and Free Particle Motion* 13
3. *The Wave Equation* 28
4. *The Wave Function and the Schrödinger Equation* 35
5. *The Linear Harmonic Oscillator* 53
6. *Piecewise Constant Potentials in One Dimension* 80
7. *The WKB Approximation* 116
8. *The Principles of Wave Mechanics* 139
9. *Central Forces and Angular Momentum* 172
10. *Piecewise Constant Potentials in Three Dimensions and the Hydrogen Atom* 191
11. *Scattering* 215
12. *The Spin* 251
13. *Dynamics of Two-Level Systems* 276
14. *Linear Vector Spaces in Quantum Mechanics* 294
15. *Quantum Dynamics* 334
16. *Rotations and Other Symmetry Operations* 371
17. *Bound State Perturbation Theory* 413
18. *Time-Dependent Perturbation Theory* 450
19. *The Formal Theory of Scattering* 488
20. *Identical Particles* 508
21. *Applications of Second Quantization* 525
22. *Photons and the Electromagnetic Field* 553
23. *Relativistic Electron Theory* 557
24. *One-Electron Dirac Theory* 591

Index 609

CHAPTER 1

Introduction to Quantum Mechanics

Quantum mechanics is the theoretical framework within which it has been found possible to describe, correlate, and predict the behavior of a vast range of physical systems, from elementary particles, through nuclei, atoms, and radiation, to molecules and solids. This introductory chapter aims at setting the stage with a brief review of the historical background and a preliminary discussion of some of the essential concepts which we shall encounter.

1. ***Quantum Theory and the Wave Nature of Matter.*** Matter at the atomic and nuclear level reveals the existence of a variety of particles which are identifiable by their distinct properties, such as mass, charge, spin, and magnetic moment. All of these seem to be of a quantum nature in the sense that they take on only certain discrete values. This discreteness of physical properties persists when elementary particles combine to form atoms and nuclei.

For instance, the notion that atoms and nuclei possess discrete energy levels is one of the basic facts of quantum physics. The experimental evidence for this fact is overwhelming and familiar. It comes most directly from observations on inelastic collisions (Franck-Hertz experiment) and selective absorption of radiation, and somewhat indirectly from the interpretation of spectral lines.

Consider as familiar an object as the hydrogen atom. The evidence that such an atom consists of a nucleus and an electron, bound to the former by forces of electrostatic attraction, is too well known to need recapitulation. The electron can be removed from the atom and identified by its charge, mass, and spin. It is equally well known that the hydrogen atom can be excited by absorbing certain discrete amounts of energy and that it can return the excitation energy by emitting light of discrete frequencies. These are empirical facts.

Niels Bohr discovered that any understanding of the observed discreteness requires, above all, the introduction of *Planck's constant*, $h = 6.6255 \times 10^{-27}$ erg sec. In old-fashioned language this constant is often called the *quantum*

of action. By the simple relation

$$\Delta E = h\nu \tag{1.1}$$

it links the observed spectral frequency ν to the jump ΔE between discrete energy levels. And, divided by 4π, the same constant appears also as the unit of angular momentum, the discrete numbers $n(h/4\pi)(n = 0, 1, 2, \ldots)$ being the only values which a component of the angular momentum of a system can assume.[1]

More specifically, Bohr was able to calculate discrete energy levels of an atom by formulating a set of quantum conditions to which the canonical variables q_i and p_i of classical mechanics were to be subjected. For our purposes it is sufficient to remember that in this "old quantum theory" the classical phase (or action) integrals for a conditionally periodic motion were required to be quantized according to

$$\oint p_i \, dq_i = n_i h \tag{1.2}$$

where the *quantum numbers* n_i are integers, and each integral is taken over the full period of the generalized coordinate q_i. The quantum conditions (1.2) give good results in calculating the energy levels of simple systems but fail when applied to such systems as the helium atom.

Exercise 1.1. Calculate the quantized energy levels of a linear harmonic oscillator of angular frequency ω in the old quantum theory.

It is well known that (1.1) played an important role even in the earliest forms of quantum theory. Einstein used it to explain the photoelectric effect by inferring that light, which through the nineteenth century had been so well established as a wave phenomenon, can exhibit a particle-like nature and is emitted or absorbed only in quanta of energy. Thus, the concept of the photon as a particle with energy $E = h\nu$ emerged. The constant h connects the wave (ν) and particle (E) aspects of light.

De Broglie proposed that the wave-particle duality may not be a monopoly of light but a universal characteristic of nature which becomes evident when the magnitude of h cannot be neglected. He thus brought out a second fundamental fact, usually referred to as the *wave nature of matter*. This means that in certain experiments beams of massive particles give rise to interference and diffraction phenomena and exhibit a behavior very similar to that of light.[2]

[1] This is true for systems which are composed of several particles (atoms, nuclei) as well as for the elementary particles themselves. Of course, these particles may be no more "elementary" than atoms and nuclei. The ease with which they can be created or destroyed and converted into each other suggests that they may be composite structures.

[2] If we sometimes speak of *matter waves*, this term is not intended to convey the impression that the particles themselves are oscillating in space.

Although such effects were first produced with electron beams, they are now commonly observed with slow neutrons from a reactor. When incident on a crystal these behave very much like X rays.

From such experiments on the diffraction of free particles we infer the very simple law that the waves associated with the motion of a particle of momentum **p** propagate in the direction of motion and that their (de Broglie) wavelength is given by

$$\lambda = \frac{h}{p} \tag{1.3}$$

This relation establishes contact between the wave and the particle pictures. The finiteness of Planck's constant is the basic point here. For if h were zero, then no matter what momentum a particle had the associated wave would always correspond to $\lambda = 0$ and would follow the laws of *classical mechanics*, which can be regarded as the short wavelength limit of *wave mechanics* in the same way as *geometrical optics* is the short wavelength limit of *wave optics*. Indeed, a free particle would then not be diffracted but go on a straight rectilinear path, just as we expect classically.

Let us formulate this a bit more precisely. If x is a characteristic length invoived in describing the motion of a body of momentum p, such as the linear dimension of an obstacle in its path, the wave aspect of matter will be hidden from our sight, if

$$\frac{\lambda}{x} = \frac{h}{xp} \ll 1 \tag{1.4}$$

i.e., if the quantum of action h is negligible compared with xp. Macroscopic bodies, to which classical mechanics is applicable, satisfy the condition $xp \gg h$ extremely well. To give a numerical example, we note that even as light a body as an atom moving with a kinetic energy corresponding to a temperature of $T = 10^{-6}$ °K still has a wavelength no greater than about 10^{-3} cm! We thus expect that classical mechanics is contained in quantum mechanics as a limiting form ($h \to 0$).

Indeed, the gradual transition which we can make conceptually as well as practically from the atomic level with its quantum laws to the macroscopic level at which the classical laws of physics are valid suggests that quantum mechanics must not only be consistent with classical physics but should yield the classical laws in a suitable approximation. This requirement, which is a guide in discovering the correct quantum laws, is called the *correspondence principle*. We shall see later that the limiting process which establishes the connection between quantum and classical mechanics can be exploited to give a useful approximation of quantum mechanical problems (see WKB approximation, Chapter 7).

We may read (1.3) the other way around and infer that any wave phenomenon also has associated with it a particle, or quantum, of momentum

$p = h/\lambda$. Hence, if a macroscopic wave is to carry an appreciable amount of momentum, as a classical electromagnetic or an elastic wave may, there must be associated with the wave an enormous number of quanta, each contributing a very small momentum. A classically observable wave will result only if the elementary wavelets representing the individual quanta add coherently. For example, the waves of the electromagnetic field are accompanied by quanta (photons) for which the relation $E = h\nu$ holds. Since photons have no mass, their energy and momentum are related by $E = cp$. It follows that (1.3) is valid for photons as well as for material particles. At macroscopic wavelengths, corresponding to radio frequency, a very large number of photons is required to build up a field of macroscopically discernible intensity. Yet, such a field can be described in classical terms only if the photons can act coherently. This requirement, which will be discussed in detail in Chapter 22, leads to the peculiar conclusion that a state of *exactly* n photons cannot represent a classical field, even if n is arbitrarily large.[3]

Exercise 1.2. To what velocity would an electron (neutron) have to be slowed down, if its wavelength is to be 1 meter? Are matter waves of macroscopic dimensions a real possibility?

2. ***Complementarity.*** As we have seen, facing us at the outset is the fact that matter, say an electron, exhibits both particle and wave aspects.[4] This duplicity of character was described in deliberately vague language by saying that the de Broglie relation (1.3) "associates" a wavelength with a particle momentum. The vagueness reflects the fact that particle and wave aspects, when they show up in the same thing such as the electron, are incompatible with each other, unless we modify our traditional concepts to a certain extent. Particle means to us traditionally an object with a definite position in space. Wave means a periodically repeated pattern in space with no particular emphasis on any one crest or valley, and it is characteristic of a wave that it does not define a location or position sharply.

How a synthesis of these two concepts might be accomplished can, for a start, perhaps be understood if we recall that the quantum theory must give an account of the discreteness of certain physical properties, e.g., energy levels in an atom or nucleus. Yet discreteness is not new in physics. In classical macroscopic physics discrete, "quantized," physical quantities appear naturally as the frequencies of vibrating bodies of finite extension, such as

[3] The massless quanta corresponding to elastic (e.g., sound) waves are called *phonons* and behave similarly to photons, except that c is now the speed of sound.

[4] It will be convenient to use the term *electron* frequently when we wish to place equal emphasis on the particle and wave aspects of a constituent of matter. The electron has been chosen only for definiteness of expression. Quantum mechanics applies equally to protons, neutrons, mesons, etc.

strings, membranes, air columns. We speak typically of the natural modes of such systems. These phenomena have found their simple explanation in terms of interference between incident and reflected waves. Mathematically the discrete behavior is enforced by boundary conditions: the fixed ends of the string, the clamping of the membrane rim, etc. It is tempting likewise to see in the discrete properties of atoms the manifestations of bounded wave motion and to connect the discrete energy levels with standing waves. In such a picture the bounded wave must somehow be related to the confinement of the particle to its "orbit," but it is obvious that the conventional concept of an orbit as a trajectory covered with definite speed cannot be maintained.

A wave is generally described by its velocity of propagation, wavelength, and amplitude. Since in a standing wave it is the *wavelength* which assumes discrete values, it is evident that, if our analogy is meaningful at all, there must be a correspondence between the energy of the particle and the wavelength of the associated wave. For a free particle, one that is not bound in an atom, the de Broglie formula (1.3) has already given us a relationship connecting wavelength with energy (or momentum). The equation linking wavelength and momentum is likely to be much more complicated for an electron bound to a nucleus as in the hydrogen atom, and it is one of our tasks to uncover the appropriate connection.

For very loosely bound electrons, moving in circular orbits far from the nucleus, (1.3) should be a good approximation. Under these circumstances the wavelength is short compared with the distance between electron and nucleus. Hence, it should be possible to describe this type of almost-free motion either as a particle moving in a well-defined classical orbit around a center of force or as a wave which can be thought of as following this orbit. From Figure 1.1 it is clear that such a situation can be described by a wave only if the orbit accommodates exactly an integral number of wavelengths (Figure 1.1*a*). Otherwise (Figure 1.1*b*) the wave is out of phase with itself, and destructive interference will prevent a stable oscillation around the nucleus. Hence, the condition for having a standing wave is

$$\oint \frac{ds}{\lambda} = n \tag{1.5}$$

the integral to be taken over the path of the trajectory. In the classical limit n is a very large integer. Using (1.3), we obtain

$$\oint p\, ds = nh \tag{1.6}$$

which for the special case of a circular orbit ($ds = r\, d\varphi$) is easily seen to be identical with a quantum condition of the form (1.2), if the aximuth φ is used as the generalized coordinate, $p_\varphi = L_z = rp$ being the canonically conjugate momentum.

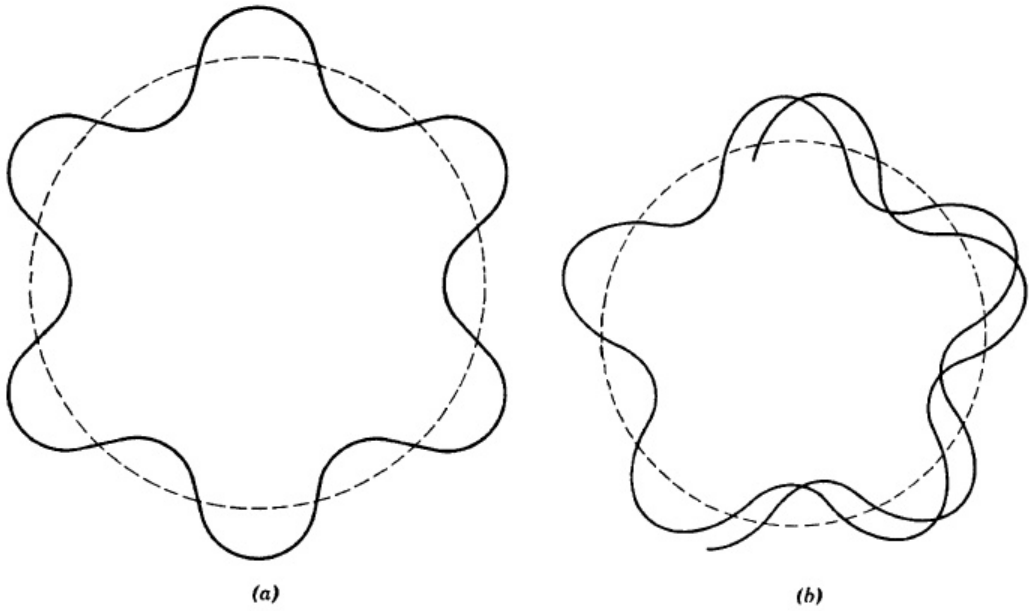


Figure 1.1. (*a*) Constructive interference of de Broglie waves in an atom distinguishes the allowed stable Bohr orbits. (*b*) Destructive interference of de Broglie waves in an atom disallows any orbit which fails to satisfy the quantum conditions.

Of course, conditions (1.2) and (1.6) are really useful and interesting only if the quantum numbers n are small integers, i.e., outside the domain of validity of the classical approximation. The bold extrapolation from large to small quantum numbers is in accordance with Bohr's demand, formulated in the correspondence principle, that a quantum equation which, like (1.6), has been established to be valid in the classical limit ($n \to \infty$) should be tentatively applied also in the unclassical quantum domain (small n). The fact that for $n = 1, 2, \ldots$ (1.6) yields the correct energy levels of the Bohr atom shows the usefulness of the correspondence principle and, more important for us, indicates that the wave-particle dualism contains the ingredients for a satisfactory description of atomic systems.

Exercise 1.3. Assuming that the electron moves in a circular orbit in a Coulomb field, derive the Balmer formula from the quantum condition (1.6).

It might be well to emphasize that the quantum conditions (1.2) or (1.6), although they give astonishingly good values for the energy levels of some quantum systems, are in general not accurate for small values of n. It should not be surprising that a naïve extrapolation from large to small quantum numbers can lead to incorrect results. The correspondence principle merely requires that quantum theory must be consistent with classical physics in the limit of large quantum numbers but does not specify uniquely the form of the

new theory. In Chapter 7 it will be shown how the old quantum conditions are obtained from quantum mechanics in a semiclassical approximation.

We owe mainly to Bohr the discovery of the principles that allow us to understand how the two seemingly contradictory concepts of wave and particle, describing the same thing, may be reconciled. We shall see in later chapters that this reconciliation requires modification of some classical attributes with which we commonly endow waves and particles. When these concepts have been appropriately broadened, one of the two pictures alone will prove inadequate for the description of physical happenings. But their new broadened definitions will—owing to a departure from the strictly classical characterizations—carry within themselves enough freedom for the two aspects to coexist. Bohr, who was guided by the empirical fact of the dual nature of matter, has elevated this program to a *principle of complementarity*. According to this principle, wave and particle nature are considered complementary aspects of matter, both equally essential for a full description of the phenomena.

It may be argued that the reasoning which has led us so far utilizes classical and conventional notions, appropriate to macroscopic phenomena but patently inapplicable in the atomic domain. After all, Bohr's quantization rules, successful as they are, entail a whole set of assumptions which are in conflict with classical physics. Chief among these is the interdiction against the emission of radiation while the electron circulates about the nucleus. This insures the stability of the Bohr orbits, but it violates classical principles concerning the radiation from accelerated charges, and it fails to help us understand the occurrence, albeit infrequently, of transitions between energy levels which give rise to the observed spectral lines. Might we not be better off if we shed all pretext of making pictures of the quantum phenomena in terms of particles and waves and the like? Why not simply establish suitable mathematical laws for the description of the observations, as Newton urged for a branch of physics reaching maturity?

Such a point of view ignores the process by which new physical theories are arrived at; new ideas always depend on understanding the novel in terms of the familiar. Of course, as the recently "new" ideas become more familiar and we become accustomed to them, the need for the older points of reference diminishes. It is for this reason, for instance, that a complete review of the elaborate calculations of the "old" quantum theory is no longer regarded as particularly helpful in the study of quantum mechanics.

Nevertheless, when all this is recognized, there still remains the possibility—according to Bohr and his Copenhagen school the necessity—that all our experience of the quantum level of nature may have to be perceived and interpreted in classical, macroscopic terms. In support of this view it is pointed out that all physical quantities such as position, momentum,

energy, angular momentum, etc., which are used in quantum mechanics as much as in classical mechanics, can be defined only by stating how they are measured. All such measurements, ultimately designed to convey information to our senses, must contain amplification mechanisms by which microscopic effects are translated into macroscopic effects accessible to our understanding. In the final analysis, atomic, nuclear, and particle experiments are all described in classical terms, since they invariably result in the reading of scales, the motion of large pointers, the activation of computer elements, etc., all of which are subject to the laws of classical physics.

According to this view, there is a subtle and profound relationship between quantum mechanics and classical physics. We have already encountered one facet of this relationship; it is the correspondence principle, which demands that quantum mechanics must be consistent with classical mechanics. Bohr went far beyond this obvious requirement and contended that quantum mechanics presupposes classical physics in a logical sense for its very formulation. Although it is not clear that this epistemological view of the relationship between classical and quantal physics and the associated doctrine of complementarity will remain central to the interpretation of quantum mechanics, an appreciation of Bohr's attitude is important because, through stimulation and provocation, it has greatly contributed to the development of the subject.

3. ***The Wave Function and Its Interpretation.*** So far we have considered only the length of matter waves, and we have found how the wavelength is connected with particle momentum. There are, of course, other important properties of these waves to be discussed. In particular, their amplitude may or may not have directional (i.e., polarization) properties. We shall see in Chapter 12 that the spin of the particles corresponds to the polarizability of the waves. However, for many purposes the dynamical effects of the spin are negligible in first approximation, especially if the particles move with nonrelativistic velocities.[5] We shall neglect the spin for the time being, much as in a simple theory of wave optical phenomena (interference, diffraction, geometrical limit, etc.) the transverse nature of light waves is neglected. Hence, we attempt to build up quantum mechanics by the use of *scalar* waves first. For particles with zero spin, e.g., pi mesons, this gives an appropriate description. For particles with nonzero spin, e.g., electrons, nucleons, mu mesons, suitable corrections must be made later (see Chapters 12 and 17).

Mathematically these waves are represented by a function $\psi(x, y, z, t)$ which in colorless terminology is called the *wave function.* Upon its introduction we immediately ask such questions as these: Is ψ a measurable quantity, and what precisely does it describe? In particular, what feature of the particle aspect is related to the wave function?

[5] This statement requires important corrections when we deal with systems of many identical particles (Chapter 20).

We cannot expect entirely satisfactory answers to these questions before we have become familiar with the properties of these waves and with the way in which ψ is used in calculations. As we progress through quantum mechanics, we shall become accustomed to ψ as an important addition to our arsenal of physical concepts. If its physical significance must as yet remain somewhat obscure to us, one thing seems certain: ψ must in some sense be a measure of the presence of a particle. Thus we do not expect to find a particle in those regions of space where $\psi = 0$. Conversely, in the regions of space where a particle may be found, ψ must be different from zero. But the function $\psi(x, y, z, t)$ itself cannot be a direct measure of the likelihood of finding a particle at position x, y, z at time t. For if it were that, it would have to be a positive number everywhere. Yet it is impossible that ψ be positive (or zero) everywhere, if destructive interference of the ψ waves is to account for the observed dark interference fringes and for the instability of any but the distinguished Bohr orbits in a hydrogen atom (Figure 1.1*b*).

In physical optics interference patterns are produced by the superposition of waves of $\mathbf{E}$ and $\mathbf{H}$, but the intensity of the fringes is measured by $\mathbf{E}^2$ and $\mathbf{H}^2$. In analogy to this situation we assume that the positive quantity $|\psi(x, y, z, t)|^2$ measures the probability of finding a particle at x, y, z. (The absolute value has been taken because it will turn out that ψ can have complex values.) The full meaning of this interpretation of ψ and its internal consistency will be discussed in detail in Chapters 4 and 8. Here we merely want to advance some general qualitative arguments for this so-called *probability interpretation* of the quantum wave function ψ. This interpretation was introduced into quantum mechanics by Born.

The discussion in the preceding section of the role that standing waves play in the hydrogen atom leads us to associate the wave ψ with a *single particle* as a representative of a statistical ensemble. The alternative would be to regard the wave as describing the behavior of a beam of particles, so that, for instance, the observed diffraction patterns would be the result of some collective phenomena. Owing to their characteristic properties, such as charge and mass, particles can, fortunately, be identified singly in the familiar detection devices of modern experimental physics: counters, bubble chambers, photographic plates, etc. With the aid of these tools it has been established abundantly that the interference fringes shown schematically in Figure 1.2 are the statistical result of the effect of a very large number of independent particles hitting the screen. The interference pattern appears only after many particles have passed through the slits, but each particle retains its discrete individuality and each goes its own way, being finally deposited somewhere on the screen. Note that the appearance of the interference effects does not require that a whole *beam* of particles go through the slits. In fact, particles can actually be accelerated and observed singly, and the interference pattern can be produced over a length of time, a particle hitting

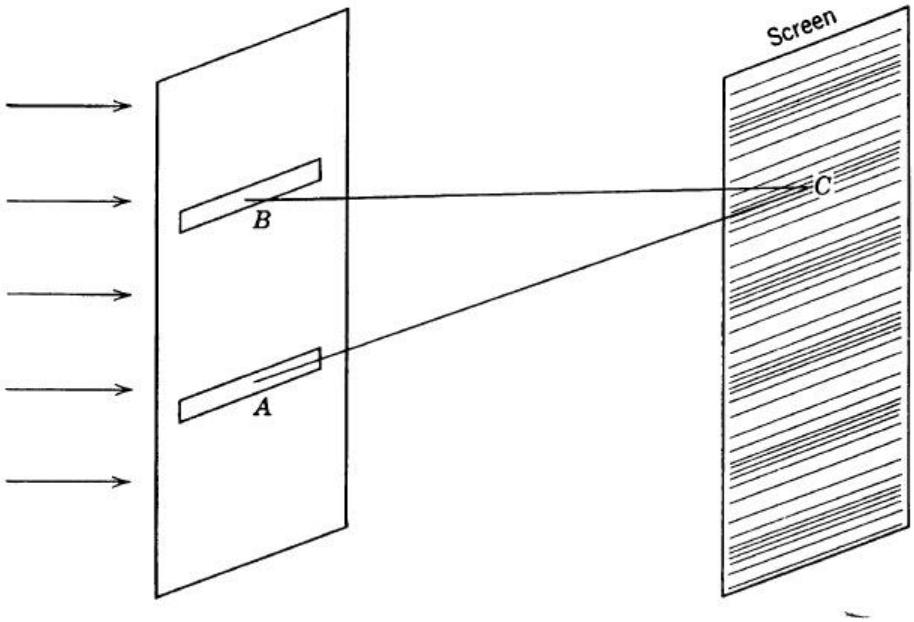


Figure 1.2. Double-slit interferences produced in analogy with Young's optical experiment. C is the location of a bright fringe on the screen if $AC - BC$ equals an integral multiple of the wavelength.

the screen now here, now there in seemingly random fashion. When many particles have come through, a regular interference pattern will be seen to have formed. The conclusion is almost inevitable that ψ describes the behavior of single particles, but that it has an intrinsic *probabilistic* meaning. The quantity $|\psi|^2$ would appear to measure the chance of finding the particle at a certain place. In a sense, this conclusion was already implicit in our earlier discussion regarding a plane wave as representative of a particle with definite momentum (wavelength) but completely indefinite position. At least if ψ is so interpreted, the observations can be correlated effortlessly with the mathematical formalism.

The opposition to the probability interpretation of ψ originates in the discomfort felt by some (including very eminent) physicists with the lack of determinism which the probabilistic view is said to ascribe to nature. The idealized experiment shown in Figure 1.2 illustrates the argument. Single particles are subject to wave interference effects, and some are found deposited on the screen at locations which they could not reach if they moved along classical paths through either slit. The appearance of the interference fringes depends on the passage of the wave through both slits at once, just as a light wave goes through both slits in the analogous optical Young interference experiment. If the wave describes the behavior of a single particle, it follows that we cannot decide through which one of the two slits the

particle has gone. If we try to avoid this consequence by determining experimentally with some clever monitoring device through which slit the particle has passed, we shall by the very action of the monitoring mechanism change the wave drastically and destroy the interference pattern. A single particle now goes definitely through one slit or the other, and the accumulation of a large number of particles on the screen will result in two well-separated traces. Exactly the same traces are obtained if we close one slit at a time, thereby predetermining the path of a particle. We conclude that the conditions under which the interference pattern is produced forbid a determination of the slit through which the particle passes.

More quantitative statements about this peculiar circumstance (Heisenberg uncertainty principle) will be made later, but the basic feature should be clear from the present example: The simultaneous appearance of wave and particle aspects compels us to be resigned to an inevitable indetermination in some of the conditions of an experiment. Wave aspect and particle aspect in one and the same thing are compatible only if we forgo asking certain questions of nature which no longer have any meaning (such as: "Let us see the interference fringes produced by particles whose paths through an arrangement of slits we have followed!"). Accepting this situation as inescapable, it is then not paradoxical to say that the interference fringes appear if the particle goes through both slits at once.

The probability doctrine of quantum mechanics asserts that the indetermination, of which we have just given an example, is a property inherent in nature and not merely a profession of our temporary ignorance from which we expect to be relieved by a future better and more complete theory. The conventional interpretation thus denies the possibility of an ideal theory which would encompass the present quantum mechanics but would be free of its supposed defects, the most notorious "imperfection" of quantum mechanics being the abandonment of strict classical determinism. Loose talk about these problems may even lead to the impression that quantum mechanics forsakes the classical goal of a wholly rational description of physical processes. Nothing could be further from the truth, as this book hopes to demonstrate.[6]

[6] Many references to the vast literature on quantum mechanics are found in the footnotes of this book. Other books that will contribute to an understanding of quantum mechanics are:

H. A. Bethe and R. W. Jackiw, *Intermediate Quantum Mechanics*, 2nd ed., W. A. Benjamin, New York, 1968.

D. Bohm, *Quantum Theory*, Prentice-Hall, New York, 1951.

P. A. M. Dirac, *The Principles of Quantum Mechanics*, 4th ed., Clarendon Press, Oxford, 1958; 1st ed.: 1930; 2nd ed.: 1935; 3rd ed.: 1947.

S. Gasiorowicz, *Elementary Particle Physics*, John Wiley and Sons, New York, 1967.

H. S. Green, *Matrix Mechanics*, P. Noordhoff Ltd., Groningen, 1965.

Footnote continued

J. M. Jauch, *Foundations of Quantum Mechanics*, Addison-Wesley Publishing Company, Reading, 1968.

L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, translated by J. B. Sykes and J. S. Bell, Addison-Wesley Publishing Company, Reading, 1958.

G. Ludwig, *Die Grundlagen der Quantenmechanik*, Springer, Berlin, 1954.

A. Messiah, *Quantum Mechanics*. Volume I translated by G. M. Temmer, Volume II translated by J. Potter, North-Holland Publishing Company, Amsterdam, 1961 and 1962.

W. Pauli, *Die allgemeinen Prinzipien der Wellenmechanik*, in S. Flügge, ed., *Encyclopedia of Physics*, vol 5/1, pp. 1–168, Springer Verlag, Berlin, 1958.

P. Roman, *Advanced Quantum Theory*, Addison-Wesley Publishing Company, Reading, 1965.

S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory*, Row, Peterson and Company, Evanston, 1961.

A. J. W. Sommerfeld, *Atombau und Spektrallinien*, Volume II, F. Vieweg, Braunschweig, 1939.

S. Tomonaga, *Quantum Mechanics*, translated by Koshiba, Volume I, North-Holland Publishing Company, 1962; Volume II, John Wiley and Sons, New York, 1966.

B. L. van der Waerden, *Sources of Quantum Mechanics*, North-Holland Publishing Company, Amsterdam, 1967.

CHAPTER 2

Wave Packets and Free Particle Motion

1. ***The Principle of Superposition.*** We have learned that it is reasonable to suppose that a free particle of momentum $\mathbf{p}$ is associated with a harmonic plane wave. Defining a vector $\mathbf{k}$ which points in the direction of wave propagation and has the magnitude

$$k = \frac{2\pi}{\lambda} \tag{2.1}$$

we may write the fundamental de Broglie relation as

$$\mathbf{p} = \hbar\mathbf{k} \tag{2.2}$$

$\hbar$ is a common symbol in quantum physics and denotes the frequently recurring constant

$$\hbar = \frac{h}{2\pi} = 1.0545 \times 10^{-27} \text{ erg sec} = 6.5819 \times 10^{-22} \text{ MeV sec}$$

It is true that the diffraction experiment does not give us any direct information about the detailed dependence on space and time of the periodic disturbance which produces the alternatingly "bright" and "dark" fringes, but all the evidence points to the correctness of the simple inferences embodied in (2.1) and (2.2). The comparison with optical interference suggests that the fringes come about by linear superposition of two waves, a point of view which has already been stressed in Section 1.3 in the discussion of the simple double-slit interference experiment, Figure 1.2.

Mathematically these ideas are formulated in the following fundamental assumption about the wave function $\psi(x, y, z, t)$: if $\psi_1(x, y, z, t)$ and $\psi_2(x, y, z, t)$ describe two waves, their sum $\psi(x, y, z, t) = \psi_1 + \psi_2$ also describes a possible physical situation. This assumption is known as the *principle of superposition* and is illustrated by the interference experiment of Figure 1.2. The intensity produced on the screen by opening only one slit at a time is $|\psi_1|^2$ or $|\psi_2|^2$. When both slits are open, the intensity is determined by

$|\psi_1 + \psi_2|^2$. This differs from the sum of the two intensities, $|\psi_1|^2 + |\psi_2|^2$ by the interference terms $\psi_1\psi_2^* + \psi_1^*\psi_2$. (An asterisk will denote complex conjugation throughout this book.)

A careful analysis of the interference experiment would require detailed consideration of the boundary conditions at the slits,[1] but there is no need here for such a thorough treatment, because our purpose in describing the idealized double-slit experiment was merely to show how the principle of superposition accounts for some typical interference and diffraction phenomena. Such phenomena, when actually observed as in diffraction of particles through crystals, are impressive direct manifestations on a macroscopic scale of the wave nature of matter.

We therefore adopt the principle of superposition to guide us in developing quantum mechanics. The simplest type of wave motion to which it will be applied is an infinite harmonic plane wave propagating in the positive x-direction with wavelength $\lambda = 2\pi/k$ and frequency ω. Such a wave is associated with the motion of a free particle moving in the x-direction with momentum $p = \hbar k$. If we followed our first impulse, we would represent this plane wave by a function of the form

$$\psi(x, t) \propto \cos(kx - \omega t + \alpha) \tag{2.3a}$$

and a plane wave moving in the negative x-direction would be written as

$$\psi(x, t) \propto \cos(kx + \omega t + \beta) \tag{2.3b}$$

The coordinates y and z can obviously be omitted in describing these one-dimensional processes.

In order to decide if (2.3*a*) and (2.3*b*) offer satisfactory means of describing plane waves in quantum mechanics, it is necessary to give some thought to the time dependence of the wave function. Classical mechanics permits the prediction of what happens at time t, if the initial conditions (coordinates and velocities) of the system at $t = 0$ are known. The correspondence principle requires that quantum mechanics must be equally deterministic and that it should be possible to calculate the condition of a system at an arbitrary time t from knowledge about it at time $t = 0$. But we have no a priori knowledge about the degree of information needed at $t = 0$, if a complete prediction of the evolution of the system is to be made, and we do not know whether the initial wave function $\psi(x, y, z, 0)$ determines $\psi(x, y, z, t)$ at all times, or whether additional information about the state at $t = 0$ is necessary.

Judging from experience with other types of wave motion, it might at first sight seem questionable that knowledge of $\psi(x, y, z, 0)$ could suffice to

[1] This is similar to the situation found in wave optics, where the uncritical use of Huygens' principle must be justified by recourse to the wave equation and to Kirchhoff's approximation.

determine $\psi(x, y, z, t)$. For example, if ψ were an elastic displacement of a vibrating string, $\partial\psi/\partial t$ would have to be specified at $t = 0$ in addition to ψ. We need only to remember that a snapshot taken of a vibrating string at $t = 0$ tells us nothing about its subsequent behavior. We must also know what it looks like a little later in order to decide whether the wave is propagating to the right, or to the left, or whether it is a standing wave. This is clearly the reason why the differential equation governing the behavior of a vibrating string must be of the *second* order in the time derivative.

As an illustration we note that the initial wave form

$$\psi(x, 0) = \cos kx \tag{2.4}$$

is obtained from either (2.3*a*) or (2.3*b*) by setting $\alpha = \beta = 0$ and $t = 0$. The initial condition (2.4) does not tell us how much of the wave travels to the right, (2.3*a*), and how much travels to the left, (2.3*b*). In fact, the wave function

$$\psi(x, t) = a \cos(kx - \omega t) + (1 - a) \cos(kx + \omega t) \tag{2.5}$$

coincides with $\psi(x, 0) = \cos kx$ at $t = 0$ for any value of a. However, knowledge of the first time derivative of (2.5) at $t = 0$

$$\left(\frac{\partial\psi}{\partial t}\right)_{t=0} = (2a - 1)\omega \sin kx$$

determines a and hence the form of (2.5) unambiguously.

We conclude that we are confronted by the following choice of working hypotheses:

I. Equations (2.3*a*) and (2.3*b*) describe plane waves, as proposed, but $\psi(x, y, z, 0)$ does not determine the wave function $\psi(x, y, z, t)$ at other times.

II. $\psi(x, y, z, 0)$ determines $\psi(x, y, z, t)$, but the expressions (2.3*a*) and (2.3*b*) do not describe simple harmonic plane ψ waves.

Since, unlike elastic displacements or electric field vectors, the ψ waves of quantum mechanics cannot be observed directly, it is tempting to construct the theory by the use of working hypothesis II and to infer from the formalism the appropriate ψ for plane waves. The only way in which we can generalize the expression (2.3*a*) for a harmonic plane wave propagating in the positive x-direction is to adjoin to the cosine a sine term, thus forming

$$\psi_1(x, t) \propto \cos(kx - \omega t) + \delta_1 \sin(kx - \omega t) \tag{2.6}$$

Similarly, a wave traveling in the opposite direction is

$$\psi_2(x, t) \propto \cos(kx + \omega t) + \delta_2 \sin(kx + \omega t) \tag{2.7}$$

The constants δ_1 and δ_2 can be determined by the requirement that the two oppositely moving plane waves ψ_1 and ψ_2 should be linearly independent at

all times,[2] and that an arbitrary displacement of x or t should not change the physical character of the wave. The linear independence insures that any harmonic plane wave can be written at all times as a linear combination of ψ_1 and ψ_2. It is then eminently reasonable to demand that the motion of a free particle moving in the positive x-direction should at all times be represented by a pure plane wave of the type ψ_1 without any admixture of ψ_2, which moves in the opposite direction. Hence, it must be required that ψ_1 at time t should be a simple multiple of ψ_1 evaluated at $t = 0$. Mathematically we must have

$$\cos(kx + \varepsilon) + \delta_1 \sin(kx + \varepsilon) = a_1(\varepsilon)(\cos kx + \delta_1 \sin kx)$$

for all values of x and ε. Comparing coefficients of $\cos kx$ and of $\sin kx$, this last equation leads to

$$\cos\varepsilon + \delta_1 \sin\varepsilon = a_1 \qquad \text{and} \qquad \delta_1 \cos\varepsilon - \sin\varepsilon = a_1\delta_1$$

These equations are compatible for all ε only if

$$\delta_1^2 = -1 \qquad \text{or} \qquad \delta_1 = \pm i$$

Similarly, from (2.7) we obtain $\delta_2^2 = -1$. We choose $\delta_1 = i$ for the wave (2.6), and $\delta_2 = -i$ for (2.7), and we are thus led to the conclusion that ψ waves describing free particle motion must be complex quantities if working hypothesis II is to succeed.

Summarizing our conclusions, we see that in this scheme a harmonic plane wave propagating toward increasing x is

$$\psi_1(x, t) = Ae^{i(kx-\omega t)} \tag{2.8}$$

and a wave propagating toward decreasing x is

$$\psi_2(x, t) = Be^{-i(kx+\omega t)} \tag{2.9}$$

The initial values of these waves are $\psi_1(x, 0) = Ae^{ikx}$ and $\psi_2(x, 0) = Be^{-ikx}$ respectively. ω is the frequency of oscillation which so far we have not brought into connection with any physically observable phenomenon. Generally, it will be a function of k (see Section 2.3). We shall refer to wave functions like (2.8) and (2.9) briefly as *plane waves.*

A plane wave propagating in an arbitrary direction has the form

$$\psi(x, y, z, t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = Ae^{i(k_x x+k_y y+k_z z-\omega t)} \tag{2.10}$$

Equations (2.8) and (2.9) are special cases of this with $k_y = k_z = 0$ and $k_x = \pm k$.

Of course, it is always possible to replace a complex wave function by two equivalent real functions (e.g., the real and imaginary parts of ψ), but to do

[2] The waves (2.3*a*) and (2.3*b*) violate this requirement. For $t = (\alpha - \beta)/2\omega$ they are equal, hence linearly dependent.

so would violate the spirit of working hypothesis II. The essence of this hypothesis is that a single function ψ determines the future state of the system. We now recognize that a price must be paid for this assumption: Complex functions ψ must be admitted. There can be at this point hardly any objection to the use of such functions. In particular, since the diffraction pattern presumably measures only the amplitude of ψ, we have no physical reason for rejecting complex-valued wave functions.

However, it should be stressed that with the acceptance of complex values for ψ we are by no means excluding wave functions which are real. For example, wave function (2.4) can be written as the sum of two exponential functions:

$$\psi(x, 0) = \cos kx = \tfrac{1}{2}e^{ikx} + \tfrac{1}{2}e^{-ikx} \tag{2.11}$$

According to the principle of superposition, this must be an acceptable wave function. How does it develop in time? The principle of superposition, in conjunction with working hypothesis II, suggests (but does not logically require) a simple answer to this important question: Each of the two waves, into which ψ can be decomposed at $t = 0$, develops independently, as if the other component were not present. The wave function, which at $t = 0$ satisfies the initial condition $\psi(x, 0) = \cos kx$, thus becomes for arbitrary t:

$$\psi(x, t) = \tfrac{1}{2}e^{i(kx-\omega t)} + \tfrac{1}{2}e^{-i(kx+\omega t)}$$

It is seen that our rule, to which we shall adhere and which we shall generalize, assures that $\psi(x, 0)$ determines the future behavior of the wave uniquely. If this formulation is correct, we shall expect that the complex ψ waves may be described by a differential equation which is of the first order in time.[3]

2. *Wave Packets and the Uncertainty Relation.* The foregoing discussion points to the possibility that by allowing the wave function to be complex we might be able to describe the state of motion of a particle at time t completely by $\psi(x, t)$. The real test of this assumption is of course its success in accounting for experimental observations. However, strong support for it can be gained by demonstrating that the correspondence with classical mechanics can be established within the framework of this theory.

To this end we must find a way of making $\psi(x, t)$ describe, at least approximately, the classical motion of a particle which has both reasonably definite position and reasonably definite momentum. The plane waves (2.8) and (2.9) correspond to particle motions with momentum which is precisely defined by

[3] Maxwell's equations are of the first order even though the functions are real, but this is accomplished by using both **E** and **B** in coupled equations, instead of describing the field by just one function. The heat flow equation is of the first order in time and still describes the behavior of a real quantity, the temperature; but none of its solutions represent waves propagating without damping in one direction like (2.10).

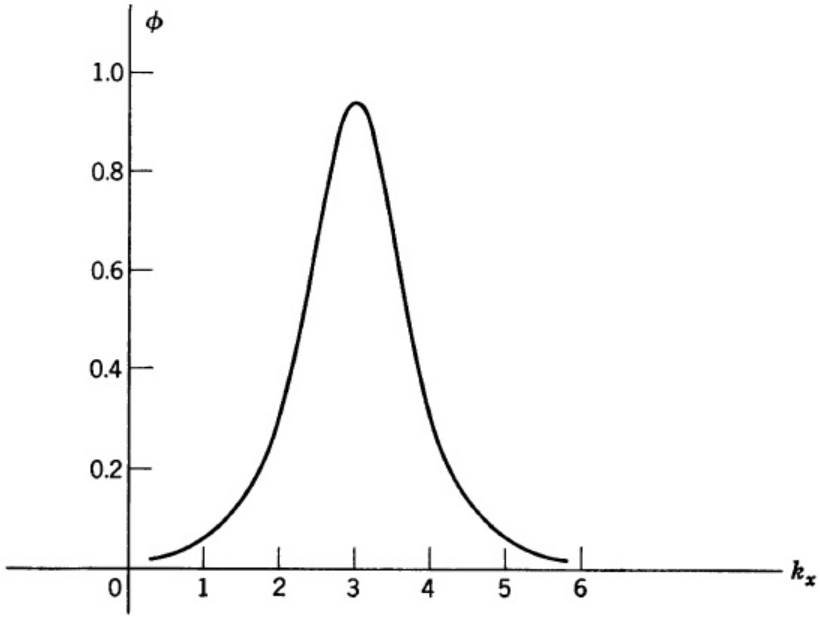


Figure 2.1. Example of a one-dimensional momentum distribution. The function $\varphi(k_x) = \pi^{1/4}[2^{1/2} \cosh \pi^{1/2}(k_x - 3)]^{-1}$ represents a wave packet moving with mean wave number $\bar{k}_x = 3$. $\varphi(k_x)$ is normalized to unity.

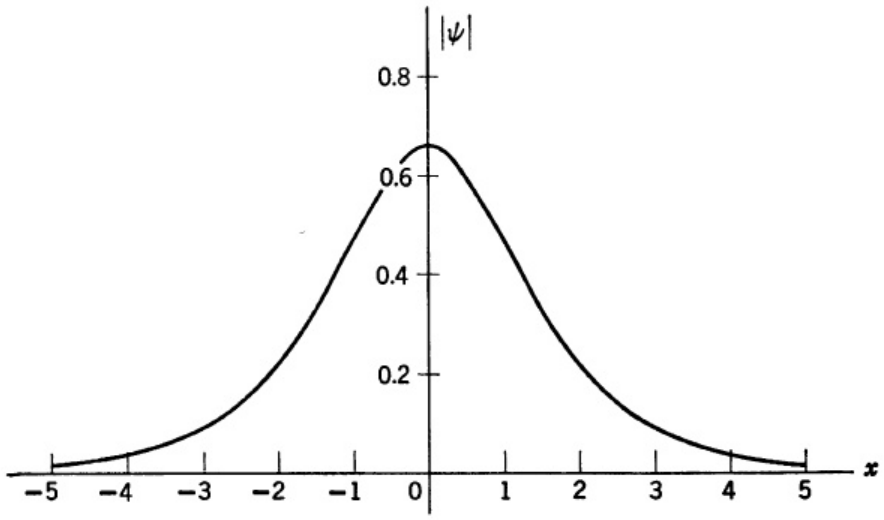


Figure 2.2. Normalized wave packet corresponding to the momentum distribution of Figure 2.1. The absolute value $|\psi(x, 0)| = \pi^{1/4}[2 \cosh (\pi^{1/2}x/2)]^{-1}$ is plotted.

(2.2); but, having amplitudes $|\psi| = \text{const.}$ for all x and t, these plane waves leave the position of the particle entirely unspecified. However, by superposition of several different plane waves a certain degree of localization can be achieved, as the fringes on the screen in the diffraction experiment attest.

The mathematical tools for such a synthesis of localized compact wave packets by the superposition of plane waves of different wave number are available in the form of *Fourier analysis*. Maintaining for simplicity the fiction that only one spatial coordinate, x, need be considered, we can write

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \varphi(k_x) e^{ik_x x}\, dk_x \tag{2.12}$$

and the inverse formula

$$\varphi(k_x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \psi(x, 0) e^{-ik_x x}\, dx \tag{2.13}$$

under very general conditions to be satisfied by $\psi(x, 0)$. Formulas (2.12) and (2.13) show that $\varphi(k_x)$ determines the initial wave function $\psi(x, 0)$, and vice versa.

We now apply the rule, established in the last section, that each component plane wave contained in (2.12) propagates independently of all the others according to the prescription of (2.10). The wave function at time t is thus:

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \varphi(k_x) e^{i(k_x x - \omega t)}\, dk_x \tag{2.14}$$

Formula (2.14) is, of course, incomplete until we determine the dependence of ω on k. This determination will be made on physical grounds in Section 2.3.

For simplicity we now assume that φ is a real positive function and that it has a shape similar to Figure 2.1, i.e., an approximately symmetric distribution of k_x about a mean value $\bar{k}_x$. Making the simple change of variables

$$u = k_x - \bar{k}_x$$

we may write

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} e^{i\bar{k}_x x} \int_{-\infty}^{+\infty} \varphi(u + \bar{k}_x) e^{iux}\, du \tag{2.15}$$

This is a wave packet whose absolute value is shown in Figure 2.2. The particle is most likely to be found at a position where ψ is appreciable. It is easy to see for any number of simple examples that the widths of the amplitude φ as a function of k_x and of the wave packet ψ stand in a reciprocal relationship:

$$\Delta x\, \Delta k_x \simeq 1 \tag{2.16}$$

A proof of this assertion will be supplied at the end of this chapter.

Exercise 2.1. Assume $\varphi(k_x) = \sqrt{2\pi}$ for $\bar{k}_x - \delta \leqslant k_x \leqslant \bar{k}_x + \delta$, and $\varphi = 0$ for all other values of k_x. Calculate $\psi(x, 0)$, plot $|\psi(x, 0)|^2$ for several values of δ and show that (2.16) holds if Δx is taken as the width at half-maximum.[4]

$\psi(x, 0)$ describes thus a particle which is localized within a distance Δx about the coordinate origin. This has been accomplished at the expense of combining waves of wave numbers in a range Δk_x about $\bar{k}_x$. The relation (2.16) shows that we can make the wave packet define a position more sharply only at the cost of broadening the spectrum of k_x-values which must be admitted. Any hope that these consequences of (2.16) might be averted by choosing $\varphi(k_x)$ more providentially has no basis in fact. On the contrary, we see easily (and we shall prove in Chapter 8 rigorously) that in general

$$\Delta x \, \Delta k_x \gtrsim 1 \tag{2.17}$$

where the $\simeq$ sign holds only if the absolute value of φ behaves as in Figure 2.1 and its phase is constant or a linear function of k_x.

Exercise 2.2. Assume $\varphi(k_x) = \sqrt{2\pi}$ for $\bar{k}_x - (\delta/2) \leqslant k_x \leqslant \bar{k}_x + (\delta/2)$, $\varphi(k_x) = -\sqrt{2\pi}$ for $\bar{k}_x - \delta \leqslant k_x < \bar{k}_x - (\delta/2)$ and for $\bar{k}_x + (\delta/2) < k_x \leqslant \bar{k}_x + \delta$, and $\varphi = 0$ for all other values of k_x. Calculate $\psi(x, 0)$ and show that, although the width of the k_x-distribution is the same as in Exercise 2.1, the width of ψ is greater in accordance with the inequality (2.17).

The fact that in quantum physics waves and particles both appear in the description of the same thing has already forced us to abandon the classical notion that position and momentum can be defined with perfect precision simultaneously. Equation (2.17) together with the equation $p_x = \hbar k_x$ expresses this characteristic property of quantum mechanics quantitatively:

$$\Delta x \, \Delta p_x \gtrsim \hbar \tag{2.18}$$

This relation suggests that when ψ is the sum of plane waves with different $\mathbf{k}$'s the wave function cannot represent a particle of definite momentum (for if it did ψ would have to be a harmonic plane wave) and that its smeared-out momentum distribution is roughly pictured by the behavior of $|\varphi|$. The particle is most likely to have the momentum $\hbar\bar{k}_x$, since φ has its greatest magnitude at $\bar{k}_x$. Obviously, we shall have to make all these statements precise and quantitative later on.

Exercise 2.3. Convince yourself that (2.18) does not in practice impose any limitations on the precision with which position and momentum of a macroscopic body can be determined.

[4] Note that if $(\Delta x)^2$ is taken to be the variance of x, as in Section 8.6, its value is infinite for the wave packets defined in Exercises 2.1 and 2.2.

For the present it suffices to view a peak in ψ as a crudely localized particle, a peak in φ as a particle moving with an approximately defined velocity. The *uncertainty relation* (2.18) limits the accuracy with which position and momentum can be simultaneously ascribed to the particle. Both quantities are fuzzy and indeterminate (*Heisenberg uncertainty principle*).

We have already discussed in Chapter 1 what this means in terms of experiments. ψ, we recall, measures roughly the *probability* of finding the particle at position x. Yet upon measurement the particle will always be found to have a definite position. Likewise, quantum mechanics does not deny that precision measurements of momentum are feasible even when the particle is not represented by a plane wave of sharp momentum. Rather, φ is a rough measure of the probability of finding the particle to have momentum $\hbar k_x$. Again we emphasize that it is not permissible to consider φ as a measure of the relative frequency of finding various values of momentum in a large assembly of particles. Instead, φ is the attribute of a single particle. Naturally, whenever a theory predicts probabilities, the experimental verification of these probabilistic predictions requires the use of large numbers of identical systems.

Under the circumstances just described, must we admit that the particle has no definite momentum (or position) when we merely are unable to determine a single value consistently in making the same measurement on identically prepared systems? Could it be that we simply have not taken sufficient precautions to ensure that the systems were in truly identical conditions before the measurement was carried out? Or is there room in the theory for supplementing the quantal description by the specification of further ("hidden") variables, so that systems which are superficially in identical states may be found to be distinct in a more refined characterization?

Quantum mechanics asserts that for any given state the measurement of a particular physical quantity results with calculable probability in a numerical value belonging to an entire range of possible measured values. It presupposes that no technical or mathematical ingenuity can devise means of giving a sharper and more accurate account of a physical state than that permitted by the wave function and the uncertainty relation. These claims constitute a principle which by its very nature cannot be proved, but which is supported extraordinarily firmly by the enormous number of verified consequences derived from it.

Bohr has shown in detail in a number of interesting thought experiments[5]

[5] See the article by Niels Bohr, "Discussion with Einstein on Epistemological Problems in Atomic Physics," in P. A. Schilpp, editor, *Albert Einstein: Philosopher-Scientist*, p. 199, Tudor Publishing Co., New York, 1957; also reprinted in N. Bohr, *Atomic Physics and Human Knowledge*, John Wiley and Sons, New York, 1958, p. 32. Other thought experiments are discussed in W. Heisenberg, *The Physical Principles of the Quantum Theory*, translated by C. Eckart and C. Hoyt, University of Chicago Press, Chicago, 1930 (Dover Publications, New York, 1949).

how the finite value of $\hbar$ in the uncertainty relation makes the coexistence of wave and particle both possible and necessary. These idealized experiments demonstrate explicitly how any effort to design a measurement of the momentum component p_x with a precision set by a number Δp_x inescapably limits the precision of a simultaneous measurement of the coordinate x to $\Delta x > \hbar/\Delta p_x$, and vice versa.

Illuminating as the thought experiments are, they merely illustrate the important discovery that underlies quantum mechanics, namely, that the behavior of a material particle is described completely by its wave function ψ (suitably modified to include the spin and other degrees of freedom, if necessary), and generally not by its precise momentum or position. Quantum mechanics contends that the wave function contains the maximum amount of information that nature allows us concerning the behavior of electrons, photons, protons, and the like.

The mathematical formalism to be developed in this book, especially in Chapters 4 and 8, and in Chapters 12 to 15, faithfully mirrors the structure of the theory that has been outlined. Energy levels, multipole moments, transition rates, and cross sections can be calculated with high precision from the the formalism, although the theory itself contains no explicit instructions for linking the mathematical elements of the theory with observable quantities. To a certain extent, the physical significance of the theory is therefore subject to *interpretation*. Various interpretations of quantum mechanics must, of course, imply the same physically verifiable deductions from the theory, but they may and do differ in the treatment of the measurement process, where tests by actual (as distinguished from thought) experiments are difficult if not impossible. All competent interpretations of quantum mechanics must thus be judged at present on the basis of internal consistency and methodological appeal. A short explicit account of the commonly accepted "*Copenhagen interpretation*" is found in Chapter 13, but the general doctrine, in a variant mostly due to von Neumann, permeates all sections of this book. It must be conceded that even this interpretation leaves some important questions unanswered and implies an unconvincing, and certainly unsubstantiated, view of the process of cognition. Fortunately, these shortcomings do not in any way inhibit the successful elaboration and application of the quantum mechanical formalism.

3. *Motion of a Wave Packet.* Having placed the wave function in the center of our considerations, we must attempt to infer as much as possible about its properties. The wave packet (2.15) which we have constructed, using the real positive function $\varphi(k_x)$ of Figure 2.1, represents a function ψ which is a plane wave of wave number $\bar{k}_x$ with an x-dependent amplitude as shown in Figure 2.2. Since in this one-dimensional case ($|k_x| = k$, $k_y = k_z = 0$) $\varphi \approx 0$ for

negative values of k_x, the mean value of the magnitude k is $\bar{k} = \bar{k}_x$. According to the correspondence principle, such a wave packet, centered around the coordinate origin, must describe classically the motion of a free particle which at $t = 0$ is at $x = 0$ and which has momentum $\hbar\bar{k}_x$ along the x-axis. Hence, the peak is expected to move according to the equation of motion

$$x_{\text{peak}} = \frac{\hbar\bar{k}_x}{\mu} t \tag{2.19}$$

where μ is the mass of the particle. The motion of the wave packet can be approximated if we expand $\omega(k)$ about $\bar{k}$,

$$\omega(k) = \omega(\bar{k}) + \left(\frac{d\omega}{dk}\right)_{k=\bar{k}} (k - \bar{k}) + \cdots = \bar{\omega} + \bar{\omega}'(k - \bar{k}) + \cdots \tag{2.20}$$

with obvious abbreviations.

For our special wave packet, which moves in the x-direction, we may set $k - \bar{k} = k_x - \bar{k}_x = u$. Assuming that we may break off the expansion with the linear term, we obtain from (2.14) and (2.15)

$$\begin{aligned} \psi(x, t) &\simeq e^{i(\bar{k}_x x - \bar{\omega} t)} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \varphi(u + \bar{k}_x) e^{iu(x - \bar{\omega}' t)}\, du \\ &= \exp(-i\bar{\omega}t + i\bar{\omega}'\bar{k}_x t)\, \psi(x - \bar{\omega}' t, 0) \end{aligned} \tag{2.21}$$

Ignoring the phase factor in front, we see that this describes a wave packet which moves without any change of shape. In particular, the peak moves with the *group velocity* $\bar{\omega}'$:

$$x = \bar{\omega}' t \tag{2.22}$$

Equations (2.19) and (2.22) are expected to be identical equations if our interpretation of the wave packet and its motion is meaningful. This equialence must hold for an arbitrary choice of $\bar{k}$. Hence, we may omit the averaging bars and require

$$\frac{d\omega}{dk} = \frac{\hbar k}{\mu}$$

Integrating this, we obtain

$$\omega = \frac{\hbar k^2}{2\mu} + \text{const.}$$

or

$$\hbar\omega = \frac{p^2}{2\mu} = \text{const.} \tag{2.23}$$

Hence, $\hbar\omega$ must be the energy of the particle, apart from an arbitrary constant which corresponds to the usual failure of nonrelativistic mechanics to give meaning to the absolute value of the energy. We may therefore assume that the particle energy E is a multiple of the frequency:

$$E = \hbar\omega \tag{2.24}$$

A similar equation has already been found to hold for photons. This is not as surprising as it may seem, for (2.2) and (2.24), although obtained in this chapter for the special case of nonrelativistic particle mechanics, are Lorentz-invariant and thus remain valid in the relativistic case. Indeed, they merely express the proportionality of two four-vectors:

$$\left(\mathbf{p}, \frac{E}{c}\right) = \hbar\left(\mathbf{k}, \frac{\omega}{c}\right) \tag{2.25}$$

Hence their great universality.

It should be noted that for the nonrelativistic case considered here the expansion (2.20) actually terminates because

$$\omega(k) = \frac{\hbar k^2}{2\mu} = \frac{\hbar \bar{k}^2}{2\mu} + \frac{\hbar \bar{k}}{\mu}(k - \bar{k}) + \frac{\hbar}{2\mu}(k - \bar{k})^2$$

Thus, if quadratic terms are retained the behavior of the wave packet is given by an exact formula.

4. *The Uncertainty Relations and the Spreading of Wave Packets.* Now we must fill some of the gaps in the mathematical detail. First, let us show that the uncertainty relation (2.16) follows from the assumed properties of φ. In order to simplify the discussion let us suppose in addition that $\varphi(k_x)$ is symmetric with respect to $\bar{k}_x$. (There is no essential loss of generality in this assumption.) The amplitude of the wave packet,

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} e^{ik_x x} \int \varphi(u + \bar{k}_x) e^{iux}\, du$$

is then symmetric about the origin. Let us denote by $(-x_0, x_0)$ the range of x for which ψ is appreciably different from zero (see Figure 2.2). Since φ is appreciably different from zero only in a range Δk_x centered at $u = 0$, the phase of e^{iux} in the integrand varies from $-x\,\Delta k_x/2$ to $+x\,\Delta k_x/2$, i.e., by an amount $x\,\Delta k_x$ for any fixed value of x. Hence the largest variations which the phase ever undergoes are $\pm x_0\,\Delta k_x$; this happens at the ends of the wave packet. If $x_0\,\Delta k_x$ is less than $\simeq 1$, no appreciable cancellations in the integrand occur (since φ is positive definite). When $x_0\,\Delta k_x \gg 1$, on the other hand, the phase goes through many periods as u ranges from $-\Delta k_x/2$ to $+\Delta k_x/2$. Hence, violent oscillations of the e^{iux} term occur, leading to destructive interference. Denoting by Δx the range $(-x_0, x_0)$, it follows that the widths of $|\psi|$ and φ are effectively related by

$$\Delta x\,\Delta k_x \simeq 1 \tag{2.16}$$

In order to prove the more general relation (2.17) we must define more precisely what is meant by the width of a function which does not have the simple behavior assumed here for φ. This will be done later (Chapter 8).

Next, we must show under what conditions it is legitimate to write the approximate equation (2.21), i.e., to neglect the quadratic term in (2.20). This quadratic term would contribute

$$\tfrac{1}{2}itu^2\left(\frac{d^2\omega}{dk^2}\right)_{k=\bar{k}}$$

to the exponent in the integrand of (2.21). An exponent can be neglected only if it is much less than unity in absolute value throughout the effective range of integration. This is assured if:

$$(\Delta k_x)^2\bar{\omega}''t \ll 1 \tag{2.26}$$

If $\omega = \hbar k^2/2\mu$, this condition becomes for nonrelativistic particles

$$t \ll \frac{\mu\hbar}{(\Delta p_x)^2} \tag{2.27}$$

or

$$t\,\Delta v_x = \frac{\Delta p_x}{\mu}\,t \ll \frac{\hbar}{\Delta p_x} \simeq \Delta x \tag{2.28}$$

$t\,\Delta v_x$ represents an uncertainty in the position of the particle at time t, over and beyond the initial uncertainty Δx. Hence, the second-order contributions to the phase can be neglected as long as the wave packet is not substantially broadened beyond its initial width. If condition (2.27) is violated, i.e., for fairly long times, our assumption about the rigid translation of the wave packet amplitude is no longer correct. It can then be shown that the quadratic term in the phase causes (2.16) to be replaced by the inequality

$$\Delta x(t)\,\Delta k_x > 1 \tag{2.29}$$

This means that the wave packet inevitably spreads, as time progresses.

Exercise 2.4. Consider a wave packet satisfying the relation $\Delta x\,\Delta p_x \simeq \hbar$. Show that if the packet is not to spread, while it passes through a fixed position, the condition $\Delta p_x \ll p_x$ must hold.

Exercise 2.5. Can the atoms in liquid helium at 4°K (interatomic distance about 1 Ångstrom) be adequately represented by nonspreading wave packets, so that their motion can be described classically?

The uncertainty relation (2.18) has a companion which relates uncertainties in time and energy. The kinetic energy is $E = p_x^2/2\mu$, and it is uncertain by an amount

$$\Delta E = \frac{p_x}{\mu}\Delta p_x = v_x\,\Delta p_x \tag{2.30}$$

If an observer is located at a fixed position, he "sees" the wave. packet sweeping through his location. His determination of the time at which the particle passes through must then be uncertain by an amount:

$$\Delta t = \frac{\Delta x}{v_x} \simeq \frac{\hbar}{v_x \Delta p_x} = \frac{\hbar}{\Delta E}$$

Hence,

$$\Delta E \, \Delta t \simeq \hbar \tag{2.31}$$

In this derivation it was assumed that the wave packet does not spread appreciably in time Δt while it passes through the observer's position. According to (2.27), this is assured if

$$\frac{\hbar}{\Delta E} \simeq \Delta t \ll \frac{\mu \hbar}{(\Delta p_x)^2}$$

With (2.30) this condition is equivalent to $\Delta E \ll E$. But the latter condition must be satisfied if we are to be allowed to speak of the energy of the particles in a beam at all.

For purposes of completeness we finally note what changes have to be made in the equations of this chapter when the restriction to motion along the x-axis is removed. The initial wave packet in three dimensions can again be Fourier-analyzed:[6]

$$\psi(x, y, z, 0) \equiv \psi(\mathbf{r}, 0) = \frac{1}{(2\pi)^{3/2}} \int \varphi(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} \, d^3k \tag{2.32}$$

and the inverse formula is

$$\varphi(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int \psi(\mathbf{r}, 0) e^{-i\mathbf{k}\cdot\mathbf{r}} \, d^3r \tag{2.33}$$

If the particle which the initial wave function (2.32) describes is free, the wave function at time t becomes

$$\psi(\mathbf{r}, t) = \frac{1}{(2\pi)^{3/2}} \int \varphi(\mathbf{k}) e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \, d^3k \tag{2.34}$$

a generalization of (2.14). ω is the same function of k as before.

If ψ is of appreciable magnitude only in the coordinate ranges Δx, Δy, Δz, then ψ is sensibly different from zero only if k_x lies in a range Δk_x, k_y in a range Δk_y, and k_z in a range Δk_z, such that

$$\Delta x \, \Delta k_x \gtrsim 1, \qquad \Delta y \, \Delta k_y \gtrsim 1, \qquad \Delta z \, \Delta k_z \gtrsim 1 \tag{2.35}$$

[6] $d^3k = dk_x \, dk_y \, dk_z$ denotes the volume element in $\mathbf{k}$-space. $d^3r = dx \, dy \, dz$ is the volume element in (position) coordinate space. For brevity the symbol of $d\tau$ will also be used for the volume element in coordinate space.

By (2.2), $\Delta \mathbf{p} = \hbar \, \Delta \mathbf{k}$; hence in three dimensions the uncertainty relations are

$$\Delta x \, \Delta p_x \gtrsim \hbar, \qquad \Delta y \, \Delta p_y \gtrsim \hbar, \qquad \Delta z \, \Delta p_z \gtrsim \hbar \tag{2.36}$$

The present chapter shows that our ideas about wave packets can be made quantitative and consistent with the laws of classical mechanics when the motion of *free* particles is considered. This is gratifying but it is not a sufficient test. Until we can show that the reasonable agreement between quantum and classical mechanics persists when forces are present, and until we demonstrate that the theory here developed yields results in accord with experiments in the atomic and nuclear domain, we cannot be entirely sure that we are on the right track.

Hence, we must now turn to an examination of the influence of forces on particle motion and wave propagation.

Problem

1. A one-dimensional initial wave packet with a mean wave number $\bar{k}_x$ and a Gaussian amplitude is given:

$$\psi(x, 0) = C \exp\left[-\frac{x^2}{4(\Delta x)^2} + i\bar{k}_x x \right]$$

Calculate the corresponding k_x-distribution and $|\psi(x, t)|^2$, and show that the wave packet advances according to the classical laws but spreads in time. Apply the results to calculate the effect of spreading in some typical microscopic and macroscopic experiments. (See also Exercises 8.13 and 15.9, and Problem 8 in Chapter 8.)

CHAPTER 3

The Wave Equation

1. ***General Remarks.*** In the last chapter we discussed what might be considered the quantum analog of Newton's first law of motion, which is a statement about the motion of free particles. Now we must find the analog of Newton's second law, describing the wave behavior of a particle which moves under the influence of forces instead of moving freely.

Two obvious requirements must be met by the dynamical law which we are seeking: (a) As the force $\mathbf{F} \to 0$, it must go over into the quantum description of the motion of a free particle, and (b) according to the correspondence principle it must embody the classical law $\mathbf{F} = \mu\mathbf{a}$, when the behavior of wave packets is described—at least when the wavelength changes relatively slowly. However, these conditions do not lead us to an unambiguous formulation of the quantum mechanics of a particle, just as in classical mechanics knowing Newton's first law, i.e., $\mathbf{a} = 0$ if $\mathbf{F} = 0$, does not allow us to infer that $\mathbf{F} \propto \mathbf{a}$ although it makes that law a possibility. Rather, experience with actual known forces and their effect on the motion of a body is needed to arrive at Newton's second law.

Unfortunately, in the case of quantum mechanics the clues which experience with actual forces gives us are not easy to interpret. The reason for this is simple: The forces which are effective in the atomic and nuclear domain, where quantum effects are measurable, are either complicated or imperfectly known, or both. The simplest such force which we know accurately is the Coulomb force by which the electrons are held to the nucleus in an atom. Here the experimental evidence consists mainly of a knowledge of the atomic spectra to very high precision and of information obtained from scattering when a charged particle collides with an atom. It is not possible to infer the general dynamical law from such data without a daring guess at some point in the sequence of reasoning. In classical mechanics it took the genius of Newton to make the leap from a mass of empirical data to a compact dynamical law. But it must not be forgotten that the immediate experience with everyday types of forces—misleading as it can be—aided Newton considerably in formulating the second law. No comparable large-scale observations were available as guides when the quantum laws were discovered.

Under these circumstances it is astounding that a single generation of physicists was able to arrive with the requisite number of bold leaps at the dynamical equations which govern the motion of particles in the quantum domain. How this was done constitutes one of the most interesting chapters in the history of physics.[1]

Equipped with all the hindsight which the reading of this history provides, we can try to justify the dynamical law of quantum mechanics without following the historical development. Of course, a certain amount of guessing is inevitable in obtaining as general a law as we are hoping for, and it would be misleading to obscure this fact by pretending that the basic equations can be *derived*. The best that can be done here is to make the final dynamical law, the wave equation of quantum mechanics, appear reasonable. A more systematic and less intuitive procedure will be used in Chapter 15.

2. *Justification of the Wave Equation.* Let us consider again a broad wave packet, representing a rather sharply defined momentum and moving from a region of space in which the particle is free toward a region in which a force is present. For simplicity we shall continue to assume a one-dimensional description.[2] We also suppose that the forces are conservative, so that classically the particle has, and maintains throughout its motion, a constant energy:

$$E = \frac{p^2}{2\mu} + V(x) \tag{3.1}$$

Accordingly, the momentum is a function of position. It is again convenient to make a Fourier decomposition of the incident wave packet:

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_0^\infty \varphi(k) e^{ikx}\, dk \tag{3.2}$$

By omitting the range of integration from $-\infty$ to 0, we have included the assumption that the wave packet moves toward positive x, and contains no negative k-components. Using the substitution

$$k = \sqrt{\frac{2\mu E}{\hbar^2}} \tag{3.3}$$

we can transform expression (3.2) into an integral over the energy of the free particle:

$$\psi(x, 0) = \int_0^\infty f(E) e^{ik(E)x}\, dE \tag{3.4}$$

[1] For an informative and readable history of quantum mechanics, see M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill Book Company, New York, 1966.

[2] Since in this chapter we confine ourselves to motion in one dimension, we drop subscripts and write p for p_x, k for k_x, etc.

$f(E)$ will be assumed to be a smoothly varying positive function of E with a single peak. Hence, (3.4) is a rather specialized wave packet, similar to that described by Figures 2.1 and 2.2. From the last chapter we know that, if this wave packet travels in force-free space, it develops in time as follows:

$$\psi(x, t) = \int f(E) \exp\left[\frac{i}{\hbar}(px - Et)\right] dE \tag{3.5}$$

We now ask: How will it move when it enters the region where a force is present?

The basic assumption which we shall make is that *the frequency is unaltered* by the approach to the region of changing potential energy. This assumption recommends itself by analogy with other types of wave motion. When a wave enters a different medium its wavelength (and its velocity of propagation) changes but the frequency of the oscillations is not affected. This behavior can usually be understood on the basis of a microscopic investigation of the structure of the medium and the simple nature of forced oscillations. Take, for instance, the case of elastic waves: If an atom of the medium vibrates with a certain frequency, the forces coupling it to its neighbors cause the neighbors to vibrate in the steady state with the same impressed frequency. (The amplitude of these vibrations depends, of course, on the proper frequencies of the atoms.)

Very similar language can be used to describe the propagation of light through a transparent refractive medium, if classical theory is used. The charges in the atoms are set into forced oscillation, *sympathetic oscillation*, as it used to be said nicely. The oscillating charges radiate with the impressed frequency, and the superposition of incident and reradiated waves results in an altered velocity of propagation.

Actually, this process requires a quantum description in which photons of the given frequency ω are absorbed and re-emitted by the atoms. Classically this means, as we have just remarked, that the atom is capable of vibrating with frequency ω, but from the particle point of view it means that the atom, owing to conservation of energy, acquires or loses energy $E = \hbar\omega$. This reasoning suggests that the relation

$$E = \hbar\omega \tag{2.24}$$

is much more universally valid than we have hitherto supposed. In a certain sense it now appears to hold also for electrons bound in atoms. Although the preceding arguments are of necessity vague and not entirely satisfactory, they indicate the general character of the theory which we are about to develop.

Of course, nothing as complicated as a theory about the interaction between light and matter is contemplated here. Rather, we are concerned with the behavior of a particle, say an electron, in a prescribed external force

field. Yet, ultimately an account must be given of the origin of any force which might act on the particle. The forces are merely shorthand expressions for the complex interactions between various wave-particle systems, which in modern physics are usually referred to as *fields*. The only example of this view of nature which has so far been almost completely elucidated is that of the electromagnetic field in interaction with charged particles. The electromagnetic forces acting between electron and proton, for instance, can in a sophisticated treatment be shown to arise as a result of the dynamical behavior of photons, the quanta of the electromagnetic field. From this point of view the constancy of the frequency of the matter waves is a consequence of the *principle of conservation of energy*, i.e., constant energy implies constant frequency according to the equation $E = \hbar\omega$.

(There is no conflict between the assumption of strict conservation of energy in the elementary interaction processes and the uncertainty relation $\Delta E\, \Delta t \gtrsim \hbar$. This relation denies the possibility of both assigning to a system a sharp value of the energy and using it as a more or less accurate time marker. The ideal condition of a system with a precisely specified energy value could only be achieved if the system were perfectly isolated and never interacted with its surroundings. The energy-time uncertainty relation is entirely consistent with the assumption that if two systems, A and B, interact, the exact amount of energy which is found to have been gained by B was lost by A, thus insuring a strict energy balance.)

In the spirit of these remarks we may compare the motion of a particle through a force field with the propagation of a wave through a strange medium whose detailed microscopic properties we do not propose to analyze here, but which can somehow be set into "sympathetic" vibrations of the same frequency and which thus interacts with the incident wave to modify its properties of propagation, i.e., its velocity of propagation and its wavelength. Always admitting that we are at best giving an approximate and partial account of physical phenomena, we conjecture that the wave packet which moves through a region of force is likely to be of the form

$$\psi(x, t) = \int f(E) \exp\left\{\frac{i}{\hbar}\left[\varphi(x, E) - Et\right]\right\} dE \tag{3.6}$$

This is a generalization of (3.5) in which $\varphi(x, E)$ is an as yet undetermined function. This function must be chosen so that (3.6) represents a wave packet which is moving classically. Since $f(E)$ is assumed to be a smooth positive function of E, the peak of the amplitude of (3.6) occurs if x and t are chosen so as to make the phase $\varphi(x, E) - Et$ stationary when $f(E)$ is near its peak. This insures that the Fourier components near the peak of $f(E)$ are as much in phase as possible and are therefore added constructively.

Mathematically, the phase is stationary if

$$\frac{\partial}{\partial E}[\varphi(x, E) - Et] = 0 \tag{3.7}$$

After differentiation, E in this equation is to be evaluated at the energy which corresponds to the peak of $f(E)$. Equation (3.7) leads to the condition

$$t = \partial\varphi/\partial E \tag{3.8}$$

On the other hand, classically for a conservative motion

$$t = \int^x \frac{dx'}{v(x')} = \int^x \frac{\partial p(x', E)}{\partial E}\, dx' \tag{3.9}$$

where $p(x, E)$ is the momentum as defined by (3.1). Comparison of (3.8) with (3.9) gives the possible choice

$$\varphi(x, E) = \int^x p(x', E)\, dx' \tag{3.10}$$

Thus we obtain

$$\psi(x, t) \simeq \int f(E) \exp\left[\frac{i}{\hbar}\left(\int^x p(x', E)\, dx' - Et\right)\right] dE \tag{3.11}$$

According to Chapter 2, (3.11) is an exact equation, instead of an approximation, if the particle is free and moves with constant momentum p corresponding to a wavelength $\lambda = h/p$. It is reasonable to assume that (3.11) is the better an approximation the more nearly $\lambda(x) = h/p(x)$ is independent of x:

$$\left|\frac{d\lambda}{dx}\right| \ll 1 \tag{3.12}$$

If this is true, the wave is quasi-harmonic and $\lambda(x)$ can be regarded as its slowly varying wavelength. Condition (3.12) can also be written as

$$h\left|\frac{dp}{dx}\right| \ll p^2 \tag{3.12a}$$

or

$$\lambda(x)\left|\frac{dV}{dx}\right| \ll \frac{[p(x)]^2}{\mu} \tag{3.12b}$$

This condition implies that the potential energy changes very little over the distance of a wavelength. The particle can then be considered as nearly free over a distance of many wavelengths, and it becomes legitimate to apply the criteria of Chapter 2 for the construction of wave packets corresponding to classical particle motion. For this reason, it will be assumed that $\hbar(dp/dx)$ can be neglected compared to p^2 in expressions derived from (3.11).

Equation (3.11) could be used to study the behavior of particles in quantum mechanics, when we are concerned with quantum corrections to the classical motion. We shall come back to this sort of approximate wave function in Chapter 7 when we discuss the WKB approximation. It suffices to point out here that some very typical quantum features are inherent in the form of ψ as given by (3.11). The most striking of these is the *penetration of a potential barrier*. Since

$$p(x, E) = \pm\sqrt{2\mu[E - V(x)]} \tag{3.13}$$

we see that an imaginary momentum results at points where $V(x) > E$. Classically, the particle cannot reach these points. Yet, if (3.11) is somewhat arbitrarily assumed to hold in this nonclassical region, the wave function does not vanish there. Hence, quantum mechanics allows for a tunneling of particles through classically inaccessible regions. Alpha decay of radioactive nuclei is the best-known example of penetration through a barrier.

One obstacle in the way of applying (3.11) extensively is that it may be quite inaccurate in regions where the kinetic energy varies rapidly with x, particularly near the classical turning points of the motion, where $p(x, E) = 0$, and where (3.12*a*) can never be satisfied. Hence, (3.11) does not provide us with an adequate formula for the description of the particle motion, where it is least classical and most interesting.

It is at this juncture that we ask ourselves whether a more generally satisfactory wave function could not be found if we abandoned the explicit construction of wave packets, which represent quite special semiclassical wave forms. A wave packet must always be given in terms of a particular initial wave $\psi(x, 0)$. Let us ask instead for some general relation which $\psi(x, t)$ must satisfy, no matter what the particular initial condition may be. Our experience with classical physics suggests that such a relation is most likely going to be a *differential equation* for $\psi(x, t)$. In fact, we are familiar with all sorts of wave equations, and the desirability of obtaining proper frequencies to account for the discrete energy spectra of atoms and nuclei suggests that one of the common types of partial differential equations, which are well known to yield discrete *eigenvalues* for appropriate boundary conditions, might be a suitable candidate. In searching for the correct equation, we are guided by the results of Chapter 2 for free particle motion. In general, we thus expect that ψ waves are complex quantities and that $\psi(x, 0)$ alone, without knowledge of the time derivative, determines the future of the wave. Hence, we shall attempt to obtain a first-order differential equation in t. It is well to admit that at this stage we are led more by analogy and guesswork than by compelling reasoning.

Following this idea, let us differentiate (3.11) with respect to time:

$$\frac{\partial \psi}{\partial t} \simeq -\int f(E)\,\frac{i}{\hbar}\,E \exp\left[\frac{i}{\hbar}\left(\int^x p\,dx' - Et\right)\right] dE \tag{3.14}$$

We would like to eliminate the initial condition $f(E)$ from the right-hand side of this equation. This can almost be accomplished if we note that

$$\frac{\partial \psi}{\partial x} \simeq \frac{i}{\hbar} \int f(E) p(x, E) \exp\left[\frac{i}{\hbar}\left(\int^x p\, dx' - Et\right)\right] dE$$

and

$$\frac{\partial^2 \psi}{\partial x^2} \simeq -\frac{1}{\hbar^2} \int f(E) p^2(x, E) \exp\left[\frac{i}{\hbar}\left(\int^x p\, dx' - Et\right)\right] dE + \frac{i}{\hbar} \int f(E) \frac{\partial p}{\partial x} \exp\left[\frac{i}{\hbar}\left(\int^x p\, dx' - Et\right)\right] dE \tag{3.15}$$

But, according to (3.12*a*) the last term is negligible compared to the first. Using (3.13), (3.14), and (3.15), we obtain, at least as an approximation,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi \tag{3.16}$$

The "bold leap" of quantization consists in asserting that this is the suitable place for going from the particular to the general and that (3.16) is valid even when (3.11) is not. In fact, we will make (3.16), the quantum mechanical *wave equation*, the basis of our theory.

CHAPTER 4

The Wave Function and the Schrödinger Equation

1. ***The Interpretation of ψ and the Conservation of Probability.*** Most of our work has so far been confined to the one-dimensional case. To insist that motion takes place in a three-dimensional space and to develop our theory accordingly would have been possible, but doing so would have required that we pay attention to details which are in no way essential to our purpose. It is far more practical to make the generalization to the case of three dimensions now that we are in possession of a partial differential equation which we believe governs the behavior of the wave function.

In Cartesian coordinates, the obvious generalization of the one-dimensional wave equation to three dimensions is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2\mu} \nabla^2 \psi + V(x, y, z)\psi \tag{4.1}$$

V is assumed to be a real function. In simple cases it represents the potential energy.[1] Since the three-dimensional space in which the particle moves is isotropic[2] and since in the absence of external forces ($V = 0$) no direction in space is preferred, (4.1) is the only possible generalization of (3.16)—short of increasing the complexity of the differential equation.

We shall adopt (4.1) as the fundamental equation of nonrelativistic quantum mechanics for particles without spin. In subsequent chapters this theory will be generalized to encompass many different and more complicated systems, but *wave mechanics*, which is the branch of quantum mechanics with a dynamical law in the explicit form (4.1), remains one of the two simplest paradigms of the general theory, the other being the dynamics of a particle with spin as its only relevant degree of freedom (Chapter 13).

The ultimate justification for choosing (4.1) must, of course, come from agreement between predictions and experiment. Hence, we must examine the

[1] See Problem 1 of this chapter for the generalization to complex V.

[2] For a precise formulation and explanation of the isotropy of space see Section 16.1.

properties of this equation. Before going into mathematical details it would, however, seem wise to attempt to say precisely what ψ is. We are in the paradoxical situation of having obtained an equation which we believe is satisfied by this quantity, but of having so far given only a deliberately vague interpretation of its physical significance. We have regarded the wave function as "a measure of the probability" of finding the particle at time t at the position $\mathbf{r}$. How can this statement be made precise?

ψ itself obviously cannot be a probability. All hopes we might have entertained in that direction vanished when ψ became a complex function, since probabilities are real and *positive*.[3] In the face of this dilemma the next best guess is that the probability is proportional to $|\psi|^2$, the square of the amplitude of the wave function. There is an analogy here to the case of optical interference where the waves whose superposition produces the interference pattern are waves of $\mathbf{E}$ and $\mathbf{H}$, but the intensity of the fringes is measured by $\mathbf{E}^2$ and $\mathbf{H}^2$, as was mentioned in Chapter 1.

Of course, we were careless when we used the phrase "probability of finding the particle *at* position $\mathbf{r}$." Actually, all we can speak of is the probability that the particle is in a volume element d^3r which contains the point $\mathbf{r}$. Hence, we now try the interpretation that $|\psi(\mathbf{r}, t)|^2\, d^3r$ is proportional to the probability that upon a measurement of its position the particle will be found in the given volume element. The probability of finding the particle in some finite region of space is proportional to the integral of $\psi^*\psi$ over this region.

Immediately doubts arise over the consistency of this probabilistic interpretation of the wave function. If the probability of finding the particle in some bounded region of space decreases as time goes on, then the probability of finding it outside of this region must increase by the same amount. The probability interpretation of the ψ waves can be made consistently only if this *conservation of probability* is guaranteed. This requirement is fulfilled, owing to Gauss' integral theorem, if it is possible to define a *probability current density* $\mathbf{j}$ which together with the *probability density* $\rho = \psi^*\psi$ satisfies a continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \tag{4.2}$$

exactly as in the case of the conservation of matter in hydrodynamics, or conservation of charge in electrodynamics.

A relation of the form (4.2) can easily be deduced from the wave equation.

[3] The solutions of (4.1) must in general be complex, because i appears explicitly in the differential equation. For $V = 0$ the quantum mechanical wave equation and the diffusion (or heat flow) equation become formally identical, but the presence of i assures that the former has solutions with wave character.

Multiply (4.1) on the left by ψ^*, and the complex conjugate of (4.1) by ψ on the right; subtract the two equations; and make a simple transformation. The resulting equation

$$\frac{\partial}{\partial t}(\psi^*\psi) + \frac{\hbar}{2\mu i}\nabla \cdot [\psi^* \nabla\psi - (\nabla\psi^*)\psi] = 0 \tag{4.3}$$

has the form of (4.2) if the identification

$$\rho = C\psi^*\psi \tag{4.4}$$

$$\mathbf{j} = C\frac{\hbar}{2\mu i}[\psi^* \nabla\psi - (\nabla\psi^*)\psi] \tag{4.5}$$

is made. C is a constant.

Exercise 4.1. Derive (4.3). Note that it depends on V being real.

Exercise 4.2. Generalizing (4.3), prove that

$$\frac{\partial}{\partial t}(\psi_1^*\psi_2) + \frac{\hbar}{2\mu i}\nabla \cdot [\psi_1^* \nabla\psi_2 - (\nabla\psi_1^*)\psi_2] = 0 \tag{4.6}$$

if ψ_1 and ψ_2 are two solutions of (4.1).

Exercise 4.3. Calculate ρ and $\mathbf{j}$ for a one-dimensional wave packet of the form (2.21) and show that in first approximation the relation

$$\mathbf{j} \simeq \frac{\bar{\mathbf{p}}}{\mu}\rho = \bar{\mathbf{v}}\rho$$

is obtained. Is this a reasonable result?

So far, we have only assumed that ρ and $\mathbf{j}$ are *proportional* to ψ and ψ^*. Since (4.1) determines ψ only to within a multiplicative constant, we may set $C = 1$,

$$\rho = \psi^*\psi \tag{4.4a}$$

$$\mathbf{j} = \frac{\hbar}{2\mu i}[\psi^* \nabla\psi - (\nabla\psi^*)\psi] \tag{4.5a}$$

and normalize the wave function by requiring

$$\int_{\text{all space}} \rho\, d\tau = \int_{\text{all space}} \psi^*\psi\, d\tau = 1 \tag{4.7}$$

provided that the integral of $\psi^*\psi$ over all space exists.[4] Equation (4.7)

[4] From here on all spatial integrations will be understood to extend over all space, unless otherwise stated, and the limits of integration will usually be omitted.

expresses the simple fact that the probability of finding the particle anywhere in space at all is unity. Whenever this integral exists we shall assume that this normalization has been imposed. Functions ψ for which $\int \psi^* \psi \, d\tau$ exists are often called *quadratically integrable.*

If the probability current density falls to zero faster than $1/r^2$ as r becomes very large and if the integral (4.7) exists, then Gauss' theorem applied to (4.2) gives

$$\frac{\partial}{\partial t} \int \rho \, d\tau = 0$$

which simply tells us that the wave equation guarantees the conservation of normalization: If ψ was normalized at $t = 0$, it will remain normalized at all times.

In the light of the foregoing remarks it is well to emphasize that throughout this book all integrals which are written down will be assumed to exist. In other words, whatever conditions ψ must satisfy for a certain integral to exist will be assumed to be met by the particular wave function used. This understanding will save us laborious repetition. Examples will occur presently.

When the integral (4.7) does *not* exist, we may use only (4.4) and (4.5), and we must then speak of *relative* rather than absolute probabilities. Wave functions which are not normalizable to unity in the sense of (4.7) are as important as normalizable ones. The former appear when the particle is unconfined, and in principle they can always be avoided by the use of finite wave packets. However, such a policy would prevent us from using such simple wave functions as the infinite plane wave e^{ikx}, which describes a particle that is equally likely to be found anywhere in space at all, hence, of course, with zero absolute probability in any finite volume. Owing to the simple properties of Fourier integrals, this patently unphysical object is mathematically extremely convenient. It is an idealization of a finite, quadratically integrable, but very broad wave packet which contains very many wavelengths. If these limitations are recognized, the infinite plane matter wave is no more objectionable than an infinite electromagnetic wave which is also unphysical, because it represents an infinite amount of energy. We shall depend on the use of such wave functions.[5]

One further comment on terminology: Since $\psi(\mathbf{r}, t)$ is assumed to contain all information about the state of the physical system at time t, the terms *wave function*, ψ, and *state* may be used interchangeably. Thus we may speak without danger of confusion of a *normalized state* if (4.7) holds.

2. *Review of Probability Concepts.* Since the interpretation of the wave function is in terms of probabilities, a brief review of probability concepts may be helpful.

[5] For the normalization of such wave functions see Sections 6.3 and 8.4.

Let us suppose that each event E_k in a set of events $E_1, E_2, \ldots$ is assigned a probability of occurrence P_k, with $\sum_k P_k = 1$. For example, in tossing a coin the two possible results, heads and tails, may be identified as event E_1 and event E_2, their probabilities being $P_1 = P_2 = 0.5$, if the coin is perfect. A variable X which takes on the value X_1 if E_1 occurs, X_2 if E_2 occurs, etc., is called a *random variable*. If in tossing the coin you are promised 1 penny for heads and 3 pennies for tails, your winnings constitute a random variable with values $X_1 = 1$, $X_2 = 3$.

The *expectation value* of X for the given probability distribution is defined to be the weighted sum

$$\langle X \rangle = \sum_k X_k P_k \tag{4.8}$$

In the example, $\langle X \rangle = 1 \times 0.5 + 3 \times 0.5 = 2$ pennies. Two pennies is the expected gain per tossing, whence the term *expectation value* for $\langle X \rangle$. (The game will be a fair one, if the ante is 2 pennies.)

If out of a large number of N trials conducted, N_1 lead to event E_1, N_2 to event E_2, etc., the relative frequencies N_k/N are expected to be approximated by the probabilities P_k. Hence, the *average value* of X, $\sum_k X_k N_k/N$, is approximately equal to the expectation value $\langle X \rangle$, and the two terms are often used synonymously. In quantum mechanics the term "expectation value" is preferred when it is desirable to emphasize the predictive nature of the theory and the fact that the behavior of a single particle is involved rather than of an ensemble of particles.

A related concept is the *variance*, $(\Delta X)^2$, of the random variable X. This is defined by

$$(\Delta X)^2 = \langle (X - \langle X \rangle)^2 \rangle = \sum_k (X_k - \langle X \rangle)^2 P_k = \langle X^2 \rangle - \langle X \rangle^2 \tag{4.9}$$

and measures the deviation from the mean. Variances will later be used for the rigorous formulation of the Heisenberg uncertainty relations (Chapter 8). In this connection we shall also encounter the (first) *correlation coefficient* of two random variables X and Y:

$$\langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle = \langle XY \rangle - \langle X \rangle \langle Y \rangle \tag{4.10}$$

If X and Y are independent (uncorrelated), the average of the product XY equals the product of the averages, $\langle X \rangle \langle Y \rangle$, and the correlation coefficient vanishes.

In this section it has been assumed that the events are discrete, whereas in the application to quantum mechanics continuous probability distributions like $|\psi|^2$ are common. The summations in (4.8) and (4.9) must then be replaced by integrations. For a normalized state the average or expectation

value of the coordinate x, which is a random variable, is

$$\langle x \rangle = \int x \, |\psi|^2 \, d\tau \tag{4.11}$$

The expectation value of the position vector, or, simply, the *center of the wave packet*, is defined by

$$\langle \mathbf{r} \rangle = \int \mathbf{r} \, |\psi|^2 \, d\tau \tag{4.12}$$

An arbitrary function of $\mathbf{r}$ has the expectation value

$$\langle f(\mathbf{r}) \rangle = \int f(\mathbf{r}) \, |\psi|^2 \, d\tau = \int \psi^* f(\mathbf{r}) \psi \, d\tau \tag{4.13}$$

The reason for writing $\langle f \rangle$ in the clumsy form $\int \psi^* f \psi \, d\tau$ will become clear when less elementary expectation values make their appearance.

3. *Expectation Values of Dynamical Variables and Operators.* Equations (4.12) and (4.13) define the expectation values of the position vector and any function thereof. The expectation values of such dynamical variables as velocity, momentum, and energy can be given equally satisfactory definitions by applying the correspondence principle. We require that the classical motion of a particle be approximated by the average behavior of a wave packet with a fairly sharp peak and as precise a momentum as the uncertainty principle permits and that the expectation values of the dynamical variables, calculated for such a wave packet, satisfy the laws of classical mechanics.

For example, we expect that the time derivative of $\langle \mathbf{r} \rangle$ will correspond to the classical velocity. This particular quantity can be calculated by the use of the continuity equation. For the x-component,

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= \int x \frac{\partial \rho}{\partial t} \, d\tau = -\int x \, \nabla \cdot \mathbf{j} \, d\tau \\ &= -\int \nabla \cdot (\mathbf{j} x) \, d\tau + \int j_x \, d\tau = \int j_x \, d\tau \end{aligned}$$

or

$$\frac{d}{dt} \langle \mathbf{r} \rangle = \int \mathbf{j} \, d\tau \tag{4.14}$$

where the divergence term has been removed under the assumption that ψ vanishes *sufficiently fast* at infinity. Using (4.5*a*) and integration by parts, we obtain finally

$$\mu \frac{d}{dt} \langle \mathbf{r} \rangle = \int \psi^* \frac{\hbar}{i} \nabla \psi \, d\tau \tag{4.15}$$

The left-hand side is simply the mass times the classical velocity. According to the assumption that expectation values are to satisfy the laws of classical mechanics, the right-hand side of (4.15) must be equal to the expectation value of the particle momentum **p**. Hence we are led to the definition

$$\langle \mathbf{p} \rangle = \int \psi^* \frac{\hbar}{i} \nabla \psi \, d\tau \tag{4.16}$$

This identification receives further support if the time rate of change of $\langle \mathbf{p} \rangle$ is considered. Using the wave equation (4.1) we find for the x-component:

$$\frac{d}{dt}\langle p_x \rangle = -i\hbar \int \frac{\partial \psi^*}{\partial t}\frac{\partial \psi}{\partial x} d\tau - i\hbar \int \psi^* \frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial t}\right) d\tau$$

$$= -\frac{\hbar^2}{2\mu}\int \left[(\nabla^2 \psi^*)\frac{\partial \psi}{\partial x} - \psi^* \nabla^2 \frac{\partial \psi}{\partial x}\right] d\tau + \int \left[V\psi^* \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial (V\psi)}{\partial x}\right] d\tau$$

The integral containing Laplacians can be transformed into a surface integral by Green's theorem.[6] It is assumed that this integral vanishes when taken over a very large surface. What remains is

$$\frac{d}{dt}\langle p_x \rangle = -\int \psi^* \frac{\partial V}{\partial x} \psi \, d\tau$$

or, more generally,

$$\frac{d}{dt}\langle \mathbf{p} \rangle = -\int \psi^* (\nabla V) \psi \, d\tau = -\langle \nabla V \rangle = \langle \mathbf{F} \rangle \tag{4.17}$$

This is simply Newton's second law, valid for expectation values, in accordance with the formulation of the correspondence principle at the beginning of this section. Equation (4.17) is known as *Ehrenfest's theorem.*

Since we have assumed conservative forces, we expect that the law of conservation of energy can also be written in terms of expectation values. It must have the form

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = \langle T \rangle + \int \psi^* V \psi \, d\tau = \text{const.}$$

but we do not yet know how to write $\langle T \rangle$ or $\langle H \rangle$ in terms of the wave function.

[6] Green's theorem for two continuously differentiable functions u and v:

$$\int_S (u \nabla v - v \nabla u) \cdot d\mathbf{S} = \int_V (u \nabla^2 v - v \nabla^2 u) \, d\tau$$

where the surface S encloses the volume V.

A glance at (4.1) shows that this problem has a simple answer: Merely multiplying (4.1) on the left by ψ^* and integrating over all space, we obtain:

$$\int \psi^* i\hbar \frac{\partial \psi}{\partial t} \, d\tau = \int \psi^* \left(-\frac{\hbar^2}{2\mu} \nabla^2 \psi \right) d\tau + \int \psi^* V \psi \, d\tau \tag{4.18}$$

By differentiating this equation with respect to t and applying the wave equation again, we find readily that the right-hand side of (4.18) is a constant of the motion. Hence, we identify the expectation value of the kinetic energy T with the expression:

$$\langle T \rangle = \int \psi^* \left(-\frac{\hbar^2}{2\mu} \nabla^2 \psi \right) d\tau \tag{4.19}$$

The expectation values (4.12), (4.13), (4.16), and (4.19) all have the same form,

$$\int \psi^* A \psi \, d\tau$$

where A is a function or differential operator which is inserted between ψ^* and ψ. The integrand is the product of ψ^* and the function $A\psi$. Generally A is termed an *operator*.

From the equations mentioned we infer the operators to be used in the calculation of expectation values given in Table 4.1. The student of quantum mechanics must get used to the confusing practice of frequently denoting the operators with which we calculate expectation values of physical quantities by the same symbols as the physical quantities themselves. This practice is unfortunate because we shall shortly encounter other formulations of quantum mechanics in which the physical quantities are represented by entirely different operators. Yet, as in most matters of notation, it is not difficult to get used to these conventions, and the context will always establish the meaning of the symbols unambiguously.

Table 4.1

Physical quantity		Operator
Position	$\mathbf{r}$	$\mathbf{r}$
Momentum	$\mathbf{p}$	$\frac{\hbar}{i} \nabla$
Kinetic energy	T	$-\frac{\hbar^2}{2\mu} \nabla^2$
Potential energy	V	$V(\mathbf{r})$
Total energy	H	$-\frac{\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r})$

Hence, we shall not hesitate to use the symbol $\mathbf{p}$ often when we really should use $(\hbar/i)\nabla$; similarly, we shall use T for $-\hbar^2\nabla^2/2\mu$. This peculiar and seemingly irresponsible identification of operators with physical quantities is encouraged by the observation that, for instance, the following operator identity holds:

$$T \equiv -\frac{\hbar^2}{2\mu}\nabla^2 = \frac{1}{2\mu}\left(\frac{\hbar}{i}\nabla\right)\cdot\left(\frac{\hbar}{i}\nabla\right) = \frac{\mathbf{p}\cdot\mathbf{p}}{2\mu} = \frac{p^2}{2\mu}$$

Thus the same relation holds between the operators T and $\mathbf{p}$ as between the classical entities known as kinetic energy and momentum. We have here a first suggestion of an alternative form of quantum mechanics in which the relations between the operators are similar to those between the corresponding classical physical quantities.[7]

All the operators listed in Table 4.1 share the property of being *linear*. An operator is said to be linear if its action on any two functions ψ_1 and ψ_2 is such that

$$A(\lambda\psi_1 + \mu\psi_2) = \lambda(A\psi_1) + \mu(A\psi_2) \tag{4.20}$$

where λ and μ are arbitrary complex numbers. Derivatives are obviously linear operators, as are mere multipliers. Most of the operators which are relevant to quantum mechanics are linear. Unless it is specifically stated that a given operator is not linear, the term *operator* will henceforth be reserved for linear operators.

The only other category of operators important in quantum mechanics are *antilinear* operators, characterized by the property

$$A(\lambda\psi_1 + \mu\psi_2) = \lambda^*(A\psi_1) + \mu^*(A\psi_2) \tag{4.20a}$$

Complex conjugation itself is an example of an antilinear operator.

Exercise 4.4. Construct some examples of linear and antilinear operators and of some operators which are neither linear nor antilinear.

4. *Stationary State Solutions.* We must now turn our attention to the wave equation and its solutions. The fundamental mathematical problem is to obtain a solution to (4.1) which for $t = 0$ agrees with a given *initial state* $\psi(\mathbf{r}, 0)$.

Since t appears nowhere explicitly in the differential equation, use of the method of separation of variables is clearly indicated. That is, we look for particular solutions of the form:

$$\psi(\mathbf{r}, t) = f(t)\psi(\mathbf{r}) \tag{4.21}$$

[7] However, it is clear that the formalism of this section is not adapted to such an approach, because an operator like $\mathbf{p} = (\hbar/i)\nabla$ does not depend on the time and could not be used in writing Newton's second law where $d\mathbf{p}/dt$ appears.

Again the use of the symbol $\psi(\mathbf{r})$ on the right-hand side of this equation for a function which is in general entirely different from $\psi(\mathbf{r}, t)$ appearing on the left-hand side is sanctioned by usage. Since this notation is very common, using a different symbol might spare the student a little confusion now but would make the reading of the literature more difficult later. Whenever necessary, care will be taken to distinguish the two functions by including the variables on which they depend.

Inserting (4.21) into (4.1), we easily obtain

$$\frac{i\hbar}{f}\frac{df}{dt} = \frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) + V\psi(\mathbf{r})\right]$$

The left-hand side of this equation depends only on t, the right-hand side only on x, y, z, hence, both must equal a constant. This constant must have the dimensions of an energy; hence, we denote it tentatively by E and obtain by integration:

$$f(t) = \exp(-iEt/\hbar) \tag{4.22}$$

On the other hand, the function $\psi(\mathbf{r})$ satisfies the equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{r}) + V\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4.23}$$

known as the *Schrödinger equation*. This equation is also called the *time-independent Schrödinger equation* in contrast to the *time-dependent Schrödinger equation* (4.1). The great importance of Equation (4.23) derives from the fact that the separation of variables yields not just some particular solution of (4.1), but generally yields *all* solutions of physical interest.

The crucial point is that under very mild boundary conditions imposed on the wave function we can prove that the separation constant E is a *real* number. The proof can be based on the continuity equation (4.2). Applying this to the state (4.21), we obtain from

$$\rho = \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = \exp\left[-\frac{i}{\hbar}(E - E^*)t\right]\psi^*(\mathbf{r})\psi(\mathbf{r})$$

upon substitution in (4.2) and integration over space:

$$(E - E^*)\int \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t)\, d\tau = \frac{\hbar}{i}\int \nabla \cdot \mathbf{j}\, d\tau = \frac{\hbar}{i}\int \mathbf{j} \cdot d\mathbf{S}$$

If the total probability flux over the boundary surface vanishes, we obtain $E = E^*$, and E must be real.

If E is real, the time-dependent factor (4.22) is purely oscillatory. Hence, in a separable state (4.21) the functions $\psi(\mathbf{r}, t)$ and $\psi(\mathbf{r})$ differ only by a time-dependent phase factor of constant amplitude. This justifies the occasional designation of the spatial factor $\psi(\mathbf{r})$ as a *time-independent wave function.*

For such a state the expectation value of any physical quantity which does not depend on time explicitly is constant and may be calculated from the time-independent wave function alone:

$$\langle A \rangle = \int \psi^*(\mathbf{r}, t) A \psi(\mathbf{r}, t)\, d\tau = \int \psi^*(\mathbf{r}) A \psi(\mathbf{r})\, d\tau \tag{4.24}$$

If the wave function (4.21) with f given by (4.22) is substituted into (4.18), the relation

$$E = \langle H \rangle = \langle T \rangle + \langle V \rangle$$

is found, showing that E is the expectation value of the total energy in this state.

We thus see that the particular solutions

$$\psi(\mathbf{r}, t) = \exp(-iEt/\hbar)\psi_E(\mathbf{r}) \tag{4.25}$$

have intriguing properties.[8] $|\psi(\mathbf{r}, t)|^2$ and all probabilities are constant in time. For this reason wave functions of the form (4.25) are said to represent *stationary states*. Note that although the state is stationary, the particle so described is in motion and not stationary at all. Also, $\nabla \cdot \mathbf{j} = 0$ for such a state.

Exercise 4.5. Further explore and discuss the properties of stationary states. Using Equation (4.6), prove the *orthogonality* relation

$$\int \psi_1^*(\mathbf{r}) \psi_2(\mathbf{r})\, d\tau = 0 \tag{4.26}$$

for any two stationary states with energies $E_1 \neq E_2$ and suitable boundary conditions.

We have already encountered one special example of a stationary state. This is the state of the *free particle* of momentum $\mathbf{p}$ and consequently of energy $E = p^2/2\mu$, i.e., the plane wave

$$\psi(\mathbf{r}, t) = \exp(-iEt/\hbar) \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar) \tag{4.27}$$

This wave function represents a state which has the definite value E for its energy. There is no uncertainty in the momentum and in the energy of this plane wave state; but there is, correspondingly, a complete ignorance of the position of the particle and of the transit time of the particle at a chosen position.

When conservative forces are introduced, the properties of momentum are, of course, drastically altered. But conservation of energy remains valid, as does—so we saw in Section 3.2—the relation according to which the

[8] The subscript E has been added in (4.25) to emphasize the time-independent factor.

energy equals $\hbar$ times the frequency. Since a stationary state (4.25) has the definite frequency $\omega = E/\hbar$, it follows that a stationary state is a state of well-defined energy, E being the definite value of its energy and not only its expectation value. This is to be understood in the sense that any determination of the energy of a particle which is in a stationary state always yields a particular value E and only that value. Such an interpretation conforms with the uncertainty relation $\Delta E\, \Delta t > \hbar$, which implies that a quantum state with a precise energy ($\Delta E = 0$) is possible only if there is unlimited time available to determine that energy. Stationary states are of just such nature in view of the constancy of $|\psi|$ in time.

The observed discrete energy levels of atoms and nuclei are approximated to a high degree of accuracy by stationary states. As will be seen in detail in Chapters 5 through 10, the simple regularity conditions which physical considerations lead us to impose on the wave function give rise in many cases to solutions of (4.23) which, instead of depending continuously on the parameter E, exist only for certain discrete values of E. This is entirely similar to the problem of a string with fixed end points, where the boundary conditions select the natural frequencies. In the quantum case, the relation $E = \hbar\omega$ associates a definite energy with every natural frequency, confirming our conclusion that the parameter E on which the stationary state wave function depends is actually *the* energy of the state. The values of E for which (4.23) has solutions consistent with the boundary conditions are said to constitute the *energy spectrum* of the Schrödinger equation. This spectrum may consist of isolated points (discrete energy levels) and continuous portions. If there is a lowest energy level, the corresponding stationary state is called the *ground state* of the system. All discrete higher energy levels are classified as *excited* states.

The reader will have noted the careful phrasing concerning the approximate nature of the connection between energy levels and stationary states. The point at issue here is that no excited state of an atom is truly discrete, stationary, and permanent. If it were, we would not see the spectral lines which result from its decay to some other level by photon emission. But the excited states are nevertheless stable to a high degree of approximation, for the period associated with an atomic state is of the order of the period of an electron moving in a Bohr orbit, i.e., about 10^{-15} sec, whereas the lifetime of the state is roughly 10^{-8} sec. Hence, during the lifetime of the state some 10^7 oscillations take place.[9] The situation is even more pronounced in the case of the so-called *unstable particles*, such as the lambda particle. Their natural periods are $\simeq 10^{-21}$ sec, their lifetimes $\simeq 10^{-10}$ sec. Thus they live for about 10^{11} periods. Comparing this with the fact that the earth has in its history completed some 10^9 revolutions around the sun—a motion which has always

[9] For a calculation of decay rates, see Chapter 22.

been considered one of the stablest—it can hardly be denied that the striking feature of the unstable particles is their stability.

5. ***General Solution of the Wave Equation.*** The stationary state wave functions are particular solutions of the wave equation. More general solutions of (4.1) can be constructed by superposition of such particular solutions. Summing over various allowed values of E, we get the solution

$$\psi(\mathbf{r}, t) = \sum_E c_E \exp\left(-\frac{i}{\hbar} Et\right) \psi_E(\mathbf{r}) \tag{4.28}$$

Here as elsewhere in this book the summation may imply an integration if a part or all of the energy spectrum of E is continuous. Furthermore, the summation in (4.28) may include the same energy value more than once. This may occur if the Schrödinger equation has more than one linearly independent solution for the same E. E is then said to be *degenerate.*

The example of the free particle in one dimension illustrates these features. In this case (4.28) becomes

$$\psi(x, t) = \sum_E c_E \exp\left(-\frac{i}{\hbar} Et\right) \exp\left(\frac{i}{\hbar} px\right) \tag{4.29}$$

There is degeneracy here, because, for any positive value of E, p can assume two values, $+\sqrt{2\mu E}$ and $-\sqrt{2\mu E}$. Since the energy spectrum is continuous and E can be any positive number, (4.29) must really be regarded as an integral. Negative values of E are excluded, because ψ would become singular for very large values of $|x|$. The exclusion of negative values of E on this ground is an example of the operation of the physically required boundary conditions.

Exercise 4.6. Show that (4.29) is equivalent to the Fourier integral (2.14).

Fourier analysis tells us that for any given initial wave packet, $\psi(x, 0)$, the expansion coefficients in (4.29) are uniquely defined. Hence, $\psi(x, t)$ in the form (4.29) is not only *a* solution of the wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi}{\partial x^2} \tag{4.30}$$

but it is the *most general* solution which can be of physical utility when describing the motion of a free particle.

In generalization of this work we see that if the Schrödinger equation yields a set of solutions $\psi_E(\mathbf{r})$ which are *complete* in the sense that any initial

state $\psi(\mathbf{r}, 0)$ of physical interest may be expanded in terms of them, i.e.,

$$\psi(\mathbf{r}, 0) = \sum_E c_E \psi_E(\mathbf{r}) \tag{4.31}$$

then we know automatically the solution of (4.1) for all t:

$$\psi(\mathbf{r}, t) = \sum_E c_E \exp\left(-\frac{i}{\hbar} Et\right) \psi_E(\mathbf{r}) \tag{4.32}$$

Thus, $\psi(\mathbf{r}, t)$ is a superposition of stationary states, if the initial wave function can be expanded in terms of solutions of the Schrödinger equation. This fact is responsible for the fundamental importance of stationary states. A discussion of the conditions under which an expansion such as (4.31) can be made will be given in Chapter 8. Here it suffices to state that the potential $V(x, y, z)$ appearing in the Schrödinger equation is usually such that the expandability of sufficiently general types of functions $\psi(\mathbf{r}, 0)$ can either be proved mathematically, as it can for the case $V = 0$, or it can be assumed to hold on physical grounds.

One more simple property of the wave equation (4.1), which can be discussed without specifying V in further detail, deserves to be mentioned. It is based on the observation that, if the complex conjugate of (4.1) is taken, and t replaced by $-t$, we get

$$i\hbar \frac{\partial \psi^*(\mathbf{r}, -t)}{\partial t} = -\frac{\hbar^2}{2\mu} \nabla^2 \psi^*(\mathbf{r}, -t) + V\psi^*(\mathbf{r}, -t) \tag{4.33}$$

provided only that V is real. This equation has the same form as (4.1). Hence, if $\psi(\mathbf{r}, t)$ is a solution of (4.1), $\psi^*(\mathbf{r}, -t)$ is also a solution. The latter is often referred to as the *time-reversed* solution of (4.1) with respect to $\psi(\mathbf{r}, t)$. The behavior of the wave equation exhibited by (4.33) is called its *invariance under time reversal.* For a stationary state, invariance under time reversal implies that, if $\psi_E(\mathbf{r})$ is a stationary wave function, $\psi_E{}^*(\mathbf{r})$ is also one. Hence, it follows that, if $\psi_E(\mathbf{r})$ is a nondegenerate solution of (4.23), $\psi_E(\mathbf{r})$ must be real, except for an arbitrary constant complex factor.

Exercise 4.7. Prove the statements of the last paragraph, and show that if degeneracy is present the solutions of the Schrödinger equation with real V may be chosen to be real.

Exercise 4.8. Prove that the Wronskian of two degenerate eigenfunctions of the one-dimensional Schrödinger equation is constant [see (4.6)].

6. *Approximate Solution of the Schrödinger Equation.* The Schrödinger equation can be regarded as the Euler-Lagrange equation for a variational problem which can be formulated as follows:

Find the functions $\psi(\mathbf{r})$ and $\psi^*(\mathbf{r})$, subject to the constraint

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})\, d\tau = 1 \tag{4.34}$$

which cause the variation of the expression

$$\langle H\rangle = \int \left(-\frac{\hbar^2}{2\mu}\,\psi^*\,\nabla^2\psi + V\psi^*\psi\right) d\tau = \int \left(\frac{\hbar^2}{2\mu}\,\nabla\psi^*\cdot\nabla\psi + V\psi^*\psi\right) d\tau \tag{4.35}$$

to vanish. It has been assumed that ψ and ψ^* satisfy certain regular boundary conditions to insure the equality of the two forms of the integral.

For an understanding of the procedure, it is sufficient to work with the one-dimensional case. According to the method of Lagrangian multipliers, the problem is equivalent to an unconstrained variational problem for the integral

$$\int F\, d\tau = \int \left(\frac{\hbar^2}{2\mu}\,\frac{d\psi^*}{dx}\,\frac{d\psi}{dx} + V\psi^*\psi - E\psi^*\psi\right) d\tau \tag{4.36}$$

where E is an as yet undetermined constant. If ψ and ψ^* are varied independently, with their conjugate relationship temporarily ignored, two differential (Euler) equations are obtained:[10]

$$\frac{\partial F}{\partial \psi^*} - \frac{d}{dx}\frac{dF}{\partial \psi^{*\prime}} = -\frac{\hbar^2}{2\mu}\,\frac{d^2\psi}{dx^2} + V\psi - E\psi = 0 \tag{4.37a}$$

$$\frac{\partial F}{\partial \psi} - \frac{d}{dx}\frac{\partial F}{\partial \psi'} = -\frac{\hbar^2}{2\mu}\,\frac{d^2\psi^*}{dx^2} + V\psi^* - E\psi^* = 0 \tag{4.37b}$$

Both of these have the form of the Schrödinger equation. Since ψ and ψ^* satisfy the appropriate regular boundary conditions, E is assured to be a real number. Hence, all equations are consistent if ψ^* is chosen as the complex conjugate of ψ.

The simultaneous use of ψ and ψ^* may seem like an unnecessary complication if V is real. However, it leads to a variational expression with a simple physical significance, since (4.35) denotes the expectation value of the energy. As the energy, this quantity has a lower bound, and the energy of the *ground state* of the system can therefore be determined as the absolute minimum of $\langle H\rangle$. Finally, the procedure described in this section is easily generalized to the Schrödinger equation for a particle in a magnetic field, which has no simple reality properties.

[10] For a review of the calculus of variations, see J. Mathews and R. L. Walker, *Mathematical Methods of Physics*, W. A. Benjamin, Inc., New York, 1964, Chapter 12.

The generalization to three dimensions is also straightforward. The solutions of the Schrödinger equation are those normalized functions ψ which render the expectation value (4.35) stationary (in the sense of the variational calculus) and equal to E. If a trial function $\psi + \delta\psi$, differing from an eigenfunction by $\delta\psi$, is used to calculate the expectation value of the energy, $E + \delta\langle H\rangle$ is obtained and, for small $\delta\psi$, the change $\delta\langle H\rangle$ is of order $(\delta\psi)^2$.

In practice, then, we can obtain various overestimates of the ground state energy by calculating $\langle H\rangle$ for suitably chosen trial functions. Obviously, altogether erroneous estimates are obtained unless the trial function is similar to the correct ground state wave function. Usually it is necessary to strike a compromise between the desire to improve the estimate of the ground state energy by choosing a "good" wave function and the requirement of ease of calculation.

The variational method is frequently applied to the Schrödinger equation of a complicated system by using for the calculation of $\langle H\rangle$ a trial wave function which contains one or more variable parameters $\alpha, \beta, \gamma, \ldots$. If the expectation value $\langle H\rangle$ is a differentiable function of these parameters, $\langle H\rangle$ is minimized (or maximized) with the help of the equations

$$\frac{\partial\langle H\rangle}{\partial\alpha} = \frac{\partial\langle H\rangle}{\partial\beta} = \frac{\partial\langle H\rangle}{\partial\gamma} = \cdots = 0$$

Evidently, the absolute minimum of $\langle H\rangle$ gives an upper limit for the lowest eigenvalue of H and may even be a fair approximation to this eigenvalue if the trial wave function is flexible enough to approximate the ground state eigenfunction ψ_0. The other, relative, extrema of $\langle H\rangle$ may correspond to excited states of the system, provided that the trial wave function is sufficiently adaptable.

As an important application, we suppose that a Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi \tag{4.38}$$

with an unmanageable potential energy V is given, but that we know the normalized solutions of a similar Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi^{(0)} + V_0\psi^{(0)} = E^{(0)}\psi^{(0)} \tag{4.39}$$

with V_0 differing from V by a small amount $\Delta V = V - V_0$. Owing to the variational property, the simple expression

$$\langle H\rangle = \int \psi^{(0)*}\left(-\frac{\hbar^2}{2\mu}\nabla^2 + V\right)\psi^{(0)}\,d\tau = E^{(0)} + \int \psi^{(0)*}\,\Delta V\psi^{(0)}\,d\tau \tag{4.40}$$

represents a sensible, and often quite accurate, estimate of the energy eigenvalue of the Schrödinger equation (4.38). The difference ΔV is called a *perturbation* of the unperturbed potential energy V_0, and the change in the energy eigenvalue

$$\Delta E = E - E^{(0)} \approx \int \psi^{(0)*} \Delta V \psi^{(0)} \, d\tau \tag{4.41}$$

is seen to be approximately equal to the expectation value of the perturbation in the unperturbed state. The formula (4.41) is the most elementary and most fundamental result of quantum mechanical *perturbation theory*.

In every physical theory two trends are evident. On the one hand, we strive to formulate exact laws and equations which govern the phenomena; on the other hand, we are confronted with the need for obtaining more or less approximate solutions to the equations, because rigorous solutions can usually be found only for oversimplified models of the physical situation. They are nevertheless useful, because they often serve as a starting point for approximate solutions to the complicated equations of the actual system.

In quantum mechanics the perturbation theories are examples of this approach. Given a complex physical system, we choose, if possible, a simpler, similar comparison system whose quantum equations can be solved rigorously. The complicated actual system may then often be described to good approximation in terms of the familiar neighboring system.

Examples of the uses of perturbation theory are legion. For instance, in atomic physics the problem of the motion of an electron in a Coulomb field can be solved rigorously (Chapter 10), and we may regard the motion of an electron in a real many-electron atom as approximated by this simpler motion, perturbed by the interaction with the other electrons. Also, the change of the energy levels of an atom in an applied electric field can be calculated by treating the field as an added perturbation and the influence of an anharmonic term in the potential energy of an oscillator on the energy spectrum can be assessed by perturbation theory (Problem 3 in Chapter 5). In fact, in a large class of practical problems in the quantum domain perturbation theory provides at least a first qualitative orientation, even where its quantitative results may be inaccurate. The formula (4.41) provides our first introduction to perturbation theory. A more systematic treatment, including the calculation of higher-order approximations, will be given in later chapters.

Problem

1. Show that the addition of an imaginary part to the potential in the quantal wave equation describes the presence of sources or sinks of probability. (Work out the appropriate continuity equation.)

Solve the wave equation for a potential of the form $V = -V_0(1 + i\zeta)$, where V_0 and ζ are positive constants. If $\zeta \ll 1$, show that there are stationary state solutions which represent plane waves with exponentially attenuated amplitude, describing absorption of the waves. Calculate the absorption coefficient.

CHAPTER 5

The Linear Harmonic Oscillator

1. ***Preliminary Remarks.*** In order to learn how to solve the Schrödinger equation and to acquire a feeling for the peculiarities of nature at the quantum level, we proceed to treat a few simple problems. As usual in theoretical physics, a great mathematical simplification results from the assumption that ψ and V depend only on the x-coordinate. The Schrödinger equation corresponding to this one-dimensional problem is an ordinary differential equation:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5.1}$$

We shall solve this equation for several special forms of the potential $V(x)$.

In this chapter the Schrödinger equation will be solved for the linear harmonic oscillator. Its potential energy is

$$V(x) = \tfrac{1}{2}\mu\omega^2 x^2 \tag{5.2}$$

We call ω loosely the (classical) frequency of the harmonic oscillator. Such a parabolic potential is actually of great practical importance, because it approximates any arbitrary potential in the neighborhood of a stable equilibrium position. $V(x)$ may be expanded in a Taylor series near $x = a$:

$$V(x) = V(a) + V'(a)(x - a) + \tfrac{1}{2}V''(a)(x - a)^2 + \cdots$$

If $x = a$ is a stable equilibrium position, $V(x)$ has a minimum at $x = a$, i.e., $V'(a) = 0$, and $V''(a) > 0$. If a is chosen as the coordinate origin and $V(a)$ as the zero of the energy scale, then (5.2) is the first approximation to $V(x)$. A familiar example is provided by the oscillations of the atoms in a diatomic molecule.

The linear harmonic oscillator is important for another reason. The behavior of most continuous physical systems, such as the vibrations of an elastic medium, or the electromagnetic field in a cavity, can be described by the superposition of an infinite number of simple harmonic oscillators. In the

quantization of any such physical system we are then confronted by the quantum mechanics of many linear harmonic oscillators of various frequencies. For this reason, all modern field theories make use of the results which we are about to obtain.

The Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \tfrac{1}{2}\mu\omega^2 x^2\psi = E\psi \tag{5.3}$$

can be transformed into a convenient form, if we substitute:

$$\xi = \sqrt{\frac{\mu\omega}{\hbar}}\, x$$

We obtain[1]

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{2E}{\hbar\omega} - \xi^2\right)\psi = 0 \tag{5.4}$$

If a power series solution of this equation is attempted, a three-term recursion formula is obtained.[2] To get a differential equation whose power series solution admits a two-term recursion relation, which is simpler to analyze, we make the substitution

$$\psi = e^{-(\xi^2/2)}v(\xi) \tag{5.5}$$

This yields the equation

$$\frac{d^2v}{d\xi^2} - 2\xi\frac{dv}{d\xi} + 2nv = 0 \tag{5.6}$$

where n is defined by the relation

$$E = \hbar\omega(n + \tfrac{1}{2}) \tag{5.7}$$

Exercise 5.1. Substituting power series with undetermined coefficients for ψ and v into (5.4) and (5.6), obtain the recursion relations and compare these.

2. *Eigenvalues and Eigenfunctions.* One simple and important property of (5.3) derives from the fact that V is an even function of x.[3] If the potential energy satisfies the condition $V(-x) = V(x)$, and if $\psi(x)$ is a solution of the

[1] By using the same symbol, ψ, in both (5.3) and (5.4) for two different functions of the variables x and ξ, we indulge in an inconsistency which, although deplorable, is sanctioned by custom.

[2] For a thorough discussion of (5.4), *Weber's equation*, see P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill Book Company, New York, 1953; also see M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards, Applied Mathematics Series 55, 1964.

[3] A function $f(x)$ is even if $f(-x) = f(x)$, and it is odd if $f(-x) = -f(x)$.

Schrödinger equation (5.1), then it follows that $\psi(-x)$ is also a solution of this equation. The Schrödinger equation with even V is said to be *invariant under reflection*, for if x is changed into $-x$, the equation is unaltered except for the replacement of $\psi(x)$ by $\psi(-x)$. Any linear combination of solutions of (5.1) also solves (5.1). Hence, if $\psi(x)$ is a solution of the Schrödinger equation, the following two functions must also be solutions:

$$\tfrac{1}{2}[\psi(x) + \psi(-x)] \tag{5.8a}$$

$$\tfrac{1}{2}[\psi(x) - \psi(-x)] \tag{5.8b}$$

These are the even and odd parts of $\psi(x)$. It is thus clear that in constructing the solutions of (5.1) we may confine ourselves to all even and all odd solutions. A state which is represented by a wave function that is even is said to have *even parity*; similarly, we speak of *odd parity* if $\psi(-x) = -\psi(x)$.

Exercise 5.2. Extend the notion of invariance under reflection (of all three Cartesian coordinates) to the Schrödinger equation in three dimensions. Show that if V depends merely on the radial distance r, only solutions of definite parity need be considered.

Since we are dealing with a linear second-order differential equation, it is easy to construct two linearly independent solutions by distinguishing two separate cases according to the "initial" conditions to be imposed:

$$\begin{aligned} &(1) \quad v_1(0) = 1, \qquad v_1'(0) = 0 \\ &(2) \quad v_2(0) = 0, \qquad v_2'(0) = 1 \end{aligned}$$

v_1 is even in ξ, v_2 is odd. By substituting

$$v_1 = 1 + a_2\xi^2 + a_4\xi^4 + \cdots$$

or

$$v_2 = \xi + a_3\xi^3 + a_5\xi^5 + \cdots$$

into (5.6) and equating the coefficient of each power of ξ to zero (see Exercise 5.1), we obtain the power series expansions

$$v_1 = 1 - \frac{2n}{2!}\xi^2 + \frac{2^2n(n-2)}{4!}\xi^4 - \frac{2^3n(n-2)(n-4)}{6!}\xi^6 + \cdots \tag{5.9a}$$

$$v_2 = \xi - \frac{2(n-1)}{3!}\xi^3 + \frac{2^2(n-1)(n-3)}{5!}\xi^5 - \cdots \tag{5.9b}$$

The rule which governs these expansions is evident.

It follows that the general solution of (5.4) is

$$\psi = e^{-(\xi^2/2)}[Av_1(\xi) + Bv_2(\xi)] \tag{5.10}$$

In order to determine if such a solution can describe a physical state or not, we must consider the asymptotic behavior of v_1 and v_2. How do these functions behave for large values of $|\xi|$? For the purpose at hand we need not become involved in complicated estimates. Unless n is an integer both series are infinite, and it suffices to establish that asymptotically $v_1 \propto e^{+\xi^2}$ and $v_2 \propto \xi e^{+\xi^2}$. Indeed, for a fixed nonintegral value of n, all coefficients from a certain one on up have the same sign, and the ratio of the coefficient of ξ^k to that of ξ^{k-2} is

$$\frac{2(k-n-2)}{k(k-1)} \to \frac{2}{k} \qquad \text{as} \qquad k \to \infty$$

But this is precisely the ratio of the coefficients of ξ^k and ξ^{k-2} in the expansion of e^{ξ^2}

Hence, unless n is an integer, v_1 behaves as e^{ξ^2} for $\xi \to \pm\infty$. v_2, on the other hand, behaves as $\pm e^{\xi^2}$ for $\xi \to +\infty$ and as $\mp e^{\xi^2}$ for $\xi \to -\infty$. Consequently, there is no conceivable choice of the coefficients A and B which would prevent $\psi(\xi)$ in (5.10) from diverging as $e^{\xi^2/2}$ either for positive or for negative large values of ξ, or both. Such wave functions are physically not useful, because they describe a situation in which it is overwhelmingly probable that the particle is not "here" but at infinity. This behavior can only be avoided if n is an integer. In this case one of the two series, (5.9*a*) or (5.9*b*), terminates and becomes a polynomial of degree n. By setting the coefficient of the other one equal to zero in (5.10), we obtain physically meaningful solutions.

If n is even we get

$$\psi = e^{-(\xi^2/2)} v_1(\xi) \tag{5.11a}$$

and the state has even parity. If n is odd we get

$$\psi = e^{-(\xi^2/2)} v_2(\xi) \tag{5.11b}$$

and the state has odd parity. Both (5.11*a*) and (5.11*b*) are now finite everywhere and quadratically integrable.

We have come to a very important conclusion: n must be a nonnegative integer ($n = 0, 1, 2, \ldots$); hence, E can assume only the discrete values $E_n = \hbar\omega(n + \frac{1}{2})$ or $E = \frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \ldots$. Classically, all nonnegative numbers are allowed for the energy of a harmonic oscillator. In quantum mechanics a stationary state of the harmonic oscillator can have only one of a discrete set of allowed energies! The energies are thus indeed quantized, and we may speak of a spectrum of *discrete energy levels* for the harmonic oscillator. The values of E or n which render the differential equation (5.3), (5.4), or (5.6) with its boundary conditions soluble are termed *eigenvalues*, and the corresponding solutions are called *eigenfunctions*. This terminology is of course not restricted to the linear harmonic oscillator but applies to the

Schrödinger equation in general. The eigenfunctions (5.11*a*) and (5.11*b*) strongly vanish at large distances, so that the particle is confined to the neighborhood of the center of force. The states described by such eigenfunctions are said to be *bound*. Note that the eigenvalues of the linear harmonic oscillator are not degenerate, since for each eigenvalue there exists only one eigenfunction, apart from an arbitrary constant factor.[4] That the eigenvalues are equidistant is one of the important peculiar features of the x^2 dependence of the oscillator potential.

The number n, whose integral values characterize and label the eigenfunctions and eigenvalues, is traditionally called a *quantum number*—a practical but not particularly sharply defined term, which we shall often use. $n = 0$ is the minimum value the quantum number n can assume and corresponds to the ground state, but the energy of the oscillator is still $\frac{1}{2}\hbar\omega$ and does not vanish as the lowest possible classical energy would. $\frac{1}{2}\hbar\omega$ is called the *zero point energy* of the harmonic oscillator. Being proportional to $\hbar$ it is obviously a quantum phenomenon, and indeed it can be understood on the basis of the uncertainty principle. Since the energy is $(p^2/2\mu) + \frac{1}{2}\mu\omega^2x^2$, zero energy would mean vanishing p *and* vanishing x, hence a precise statement of both the coordinate and the momentum of the particle.[5] This would be in conflict with the uncertainty relation.

3. ***Study of the Eigenfunctions.*** In this section a few important mathematical properties of the harmonic oscillator eigenfunctions will be derived.

The finite polynomial solutions of (5.6) which can be constructed if n is an integer are known as *Hermite polynomials* of degree n. The complete eigenfunctions are of the form

$$\psi_n(x) = C_n H_n\left(\sqrt{\frac{\mu\omega}{\hbar}}\, x\right) \exp\left(-\frac{\mu\omega}{2\hbar}\, x^2\right) \tag{5.12}$$

where H_n denotes a Hermite polynomial of degree n, and C_n is an as yet undetermined normalization constant. But first the Hermite polynomials themselves must be normalized. It is traditional to define them so that the highest power of ξ appears with the coefficient 2^n. Hence, for even n

$$H_n(\xi) = (-1)^{n/2}\, \frac{n!}{(n/2)!}\, v_1(\xi) \tag{5.13a}$$

[4] This property is common to bound states in one-dimensional problems, provided that the potential is finite at finite values of x. Even if the particle is confined only from one side, there is still no degeneracy in one dimension.

[5] At first sight the argument given here may seem unsatisfactory, because it uses x and p as if they were classical variables, when really they are operators. However, the argument can be made rigorous by using expectation values. See Section 8.6 and Problem 4 in Chapter 8.

and for odd n

$$H_n(\xi) = (-1)^{(n-1)/2} \frac{2(n!)}{[(n-1)/2]!} v_2(\xi) \tag{5.13b}$$

Here is a list of the first few Hermite polynomials:

$$\begin{aligned} H_0(\xi) &= 1 & H_3(\xi) &= -12\xi + 8\xi^3 \\ H_1(\xi) &= 2\xi & H_4(\xi) &= 12 - 48\xi^2 + 16\xi^4 \\ H_2(\xi) &= -2 + 4\xi^2 & H_5(\xi) &= 120\xi - 160\xi^3 + 32\xi^5 \end{aligned} \tag{5.14}$$

The first few harmonic oscillator eigenfunctions are plotted in Figure 5.1. They satisfy the differential equation

$$\frac{d^2H_n}{d\xi^2} - 2\xi \frac{dH_n}{d\xi} + 2nH_n = 0 \tag{5.15}$$

Exercise 5.3. By differentiating (5.15), prove that

$$\frac{dH_n(\xi)}{d\xi} = 2nH_{n-1}(\xi) \tag{5.16}$$

A particularly simple representation of the Hermite polynomials is obtained by constructing the function

$$F(s, \xi) = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n \tag{5.17}$$

As a consequence of (5.16), we see that

$$\frac{\partial F}{\partial \xi} = 2sF$$

This differential equation can be integrated:

$$F(s, \xi) = F(s, 0)e^{2s\xi}$$

The coefficient $F(s, 0)$ can be evaluated from (5.17) and (5.13):

$$F(s, 0) = \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} s^{2k} = e^{-s^2}$$

and therefore the *generating function* $F(s, \xi)$ has the form

$$F(s, \xi) = e^{-s^2+2s\xi} = e^{\xi^2-(s-\xi)^2} \tag{5.18}$$

The generating function $F(\xi, s)$ is very useful because it allows us to deduce a number of simple properties of the harmonic oscillator wave functions with

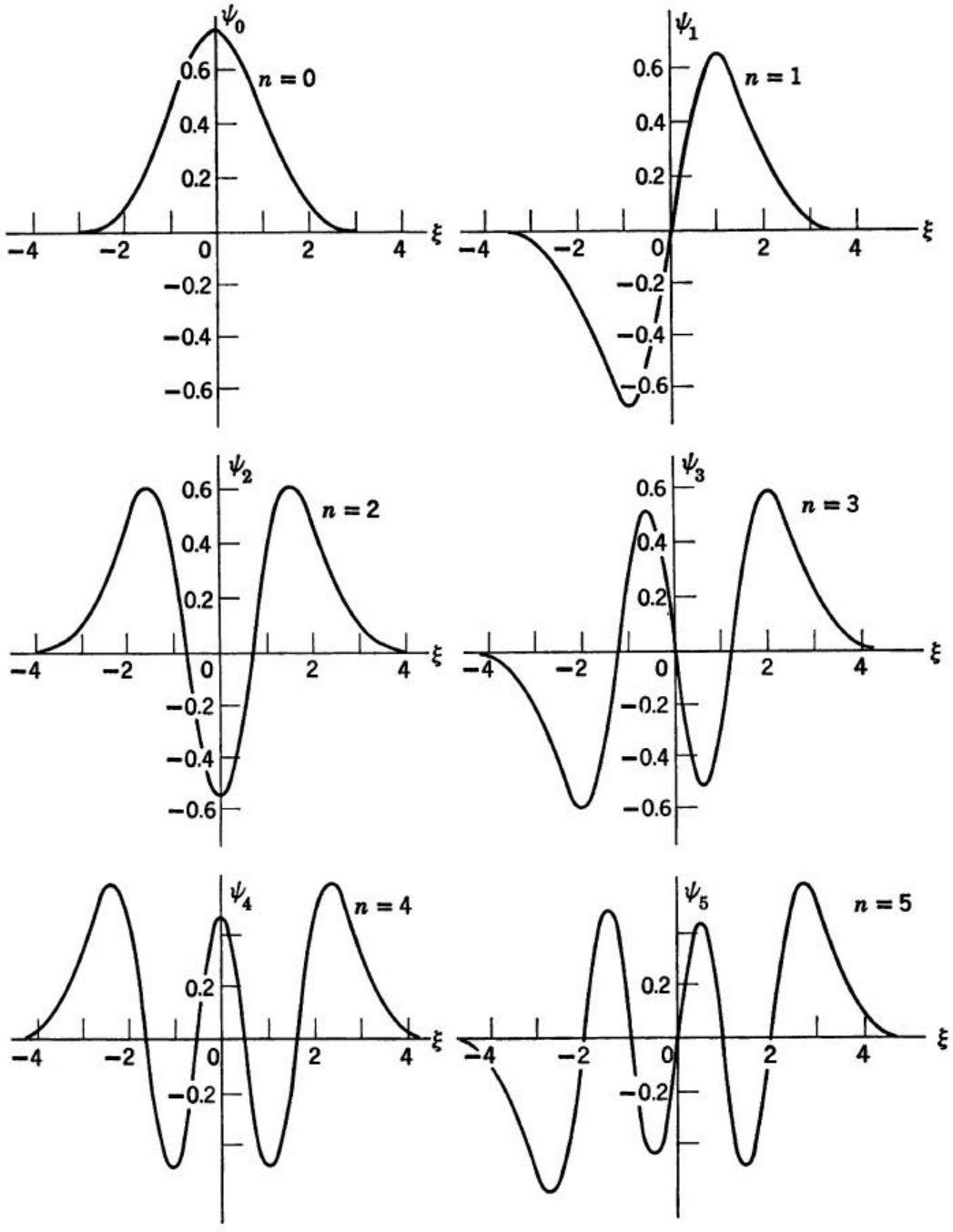


Figure 5.1. The eigenfunctions of the linear harmonic oscillator for the quantum numbers $n = 0$ to 5. ψ_n is plotted versus $\xi = \sqrt{\mu\omega/\hbar}\, x$, and all eigenfunctions are normalized as $\int_{-\infty}^{+\infty} |\psi_n(\xi)|^2 \, d\xi = 1$.

great ease. For example, by Taylor's expansion:

$$H_n(\xi) = \left[\frac{d^n}{ds^n} e^{\xi^2-(s-\xi)^2}\right]_{s=0} = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} \tag{5.19}$$

a popular alternative form of definition of the Hermite polynomials.

From this definition it follows that all n roots of $H_n(\xi)$ must be real.

Proof. Assume that $d^{n-1}e^{-\xi^2}/d\xi^{n-1}$ has $n-1$ real roots. Since $e^{-\xi^2}$ and all its derivatives tend to zero as $\xi \to +\infty$ and $-\infty$, the derivative $d^n e^{-\xi^2}/d\xi^n$ must have at least n real roots. Being $e^{-\xi^2}$ times a polynomial, it can have no more than n such roots. The assumption holds for $n = 1$, whence the assertion follows by induction.

The points in space at which a wave function goes through zero are called its *nodes*. Evidently, the oscillator eigenfunction (5.12) has n nodes.

A very important property of the Hermite polynomials is their orthogonality in the sense that for $n \neq k$

$$\int_{-\infty}^{+\infty} H_n(\xi) H_k(\xi) e^{-\xi^2} d\xi = 0 \tag{5.20}$$

It is convenient and economical to prove a rather more general formula by the use of the generating function. To this end we construct the expression

$$\int_{-\infty}^{+\infty} e^{\xi^2-(s-\xi)^2} e^{\xi^2-(t-\xi)^2} e^{2\lambda\xi-\xi^2} d\xi = \sum_{n=0}^{\infty}\sum_{k=0}^{\infty} \frac{s^n t^k}{n!\,k!} \int_{-\infty}^{+\infty} H_n(\xi) H_k(\xi) e^{2\lambda\xi-\xi^2} d\xi$$

where (5.17) and (5.18) have been used. The left-hand side can be integrated explicitly; it equals

$$e^{2st+\lambda^2+2\lambda(s+t)} \int_{-\infty}^{+\infty} e^{-(s+t+\lambda-\xi)^2} d\xi = \sqrt{\pi}\, e^{\lambda^2+2(st+\lambda s+\lambda t)}$$

Comparing the coefficients of equal powers of $s^n t^k \lambda^p$, we obtain the value of a useful integral:

$$\int_{-\infty}^{+\infty} H_n(\xi) H_k(\xi) e^{-\xi^2} \xi^p\, d\xi \tag{5.21}$$

In particular, for $p = 0$ and $n \neq k$, the orthogonality relation (5.20) is derived. For $p = 0$ and $n = k$ we obtain the integral

$$\int_{-\infty}^{+\infty} [H_n(\xi)]^2 e^{-\xi^2} d\xi = 2^n n! \sqrt{\pi} \tag{5.22}$$

If we recall that $\xi = \sqrt{\mu\omega/\hbar}\, x$, (5.20) and (5.22) can be written more simply

in terms of the normalized eigenfunctions (5.12), and we have

$$\int_{-\infty}^{+\infty} \psi_n^*(x)\, \psi_k(x)\, dx = \delta_{nk} \tag{5.23}$$

if the normalization constant is chosen properly. A set of eigenfunctions satisfying relation (5.23) is said to be *orthonormal*. The orthonormal oscillator eigenfunctions are

$$\psi_n(x) = 2^{-n/2}(n!)^{-1/2}\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{\mu\omega}{2\hbar}x^2\right) H_n\left(\sqrt{\frac{\mu\omega}{\hbar}}\,x\right) \tag{5.24}$$

In (5.23) complex conjugation appears, although with the particular choice of the arbitrary phase factor embodied in (5.24) the eigenfunctions are real. However, in the form given, (5.23) is an example of the general orthogonality relation (4.26) for the eigenfunctions of the Schrödinger equation.

4. ***The Motion of Wave Packets.*** So far we have considered only the stationary states of the harmonic oscillator. We must now turn our attention to the behavior of a general wave $\psi(x, t)$ whose initial form $\psi(x, 0)$ is given. The wave equation

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2\mu}\frac{\partial^2\psi(x,t)}{\partial x^2} + \tfrac{1}{2}\mu\omega^2x^2\psi(x,t)$$

determines the time development of the wave. In Chapter 4 we saw that the solution of this equation can be obtained automatically, if the initial wave can be expanded in terms of the time-independent eigenfunctions of the corresponding Schrödinger equation. For the linear harmonic oscillator this is indeed possible to an approximation which can be made as close as we please.

To see this, we must ask whether an arbitrary initial wave function $\psi(x, 0)$ can be expanded as

$$\psi(x, 0) = \sum_{n=0}^{\infty} c_n C_n \exp\left(-\frac{\mu\omega}{2\hbar}x^2\right) H_n\left(\sqrt{\frac{\mu\omega}{\hbar}}\,x\right)$$

where C_n denotes the normalization constant given in (5.24).

It is convenient to transfer the exponential factor to the left side of the equation and to look at the function

$$\psi(x, 0) \exp\left(\mu\omega x^2/2\hbar\right) \tag{5.25}$$

Since x^n can always be expressed as a linear combination of the first $n + 1$ Hermite polynomials, it is seen that any function (5.25) which is analytic (i.e., can be expanded in a power series) can also be expanded in terms of Hermite polynomials.

Actually, a much larger class of functions can be expanded as

$$\psi(x, 0) = \sum_{n=0}^{\infty} c_n \psi_n(x) \tag{5.26}$$

if the notion of convergence is suitably relaxed. This will be discussed in Chapter 8. In any event, a finite number of terms in (5.26) approximates most physically pertinent initial wave packets very well.[6] Owing to the orthonormality, (5.26) gives us

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x)\psi(x, 0)\, dx \tag{5.27}$$

If $\psi(x, 0)$ is normalized, the orthonormality of the eigenfunctions causes the expansion coefficients to satisfy the simple normalization relation

$$\sum_{n=0}^{\infty} |c_n|^2 = 1 \tag{5.28}$$

With these expansion coefficients and with $E_n = \hbar\omega(n + \frac{1}{2})$ we can now construct the wave packet at time t by the use of (4.28):

$$\psi(x, t) = \exp\left(-\frac{i\omega}{2}t\right) \sum_{n=0}^{\infty} c_n \psi_n(x) \exp(-in\omega t) \tag{5.29}$$

The expectation value of the energy in this state can be calculated from (4.18):

$$\langle H \rangle = \int_{-\infty}^{+\infty} \psi^*(x, t)\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \tfrac{1}{2}\mu\omega^2 x^2\right)\psi(x, t)\, dx \tag{5.30}$$

Substituting the expansion (5.29) into (5.30) and using the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \tfrac{1}{2}\mu\omega^2 x^2\right)\psi_n(x) = E_n \psi_n(x)$$

as well as the orthonormality relation (5.23), we obtain

$$\langle H \rangle = \sum_{n=0}^{\infty} E_n |c_n|^2 \tag{5.31}$$

Equations (5.28) and (5.31) taken together suggest an important and straightforward extension of the probability interpretation of quantum mechanics. These relations are in accord with the assumptions that

[6] The ambiguous phrase "... approximates ... physically pertinent ... very well" will be made precise in Chapter 8.

(a) the only possible results of measuring the energy of the system are the energy values $E_0, E_1, \ldots, E_n, \ldots$, and

(b) if the system is in state $\psi(x, t)$, the probability of obtaining the result E_n is equal to $|c_n|^2$.

These assumptions, which will find their proper place later in the general formulation of quantum mechanics, can be given further support by considering the motion of the wave packet in more detail.

The center of probability of the normalized wave packet, i.e., the expectation value of the position operator x, is according to (4.11)

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \, |\psi(x, t)|^2 \, dx \tag{5.32}$$

Substituting (5.29) into (5.32) we find

$$\langle x \rangle = \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} c_n^* c_k e^{i(n-k)\omega t} \int_{-\infty}^{+\infty} \psi_n^*(x) \, x \, \psi_k(x) \, dx \tag{5.33}$$

We see here that it is important to know the numbers

$$x_{nk} = \int_{-\infty}^{+\infty} \psi_n^*(x) \, x \, \psi_k(x) \, dx \tag{5.34}$$

As we shall see later in detail, the square array

$$\begin{pmatrix} x_{00} & x_{01} & x_{02} & \cdot & \cdot \\ x_{10} & x_{11} & x_{12} & \cdot & \cdot \\ x_{20} & x_{21} & x_{22} & \cdot & \cdot \\ x_{30} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \tag{5.35}$$

formed by these numbers can be used conveniently as a matrix representing the operator x. In anticipation of these results we call the quantities x_{nk} the *matrix elements* of x.

Let us evaluate these matrix elements explicitly. Evidently

$$\begin{aligned} x_{nk} &= 2^{-(n+k)/2}(n!)^{-1/2}(k!)^{-1/2}\left(\frac{\mu\omega}{\hbar\pi}\right)^{1/2} \\ &\quad \times \int_{=\infty}^{+\infty} \exp\left(-\frac{\mu\omega}{\hbar} x^2\right) H_n\left(\sqrt{\frac{\mu\omega}{\hbar}}\, x\right) x \, H_k\left(\sqrt{\frac{\mu\omega}{\hbar}}\, x\right) dx \\ &= \sqrt{\frac{\hbar}{\mu\omega}}\, 2^{-(n+k)/2}(n!)^{-1/2}(k!)^{-1/2}\pi^{-1/2} \int_{-\infty}^{+\infty} H_n(\xi) H_k(\xi) \xi e^{-\xi^2} \, d\xi \end{aligned}$$

By specializing (5.21) to $p = 1$, we obtain

$$\int_{-\infty}^{+\infty} H_n(\xi)H_k(\xi)\xi e^{-\xi^2}\,d\xi = \sqrt{\pi}\,2^{n-1}n!\,[\delta_{k,n-1} + 2(n+1)\delta_{k,n+1}]$$

Hence,

$$x_{nk} = \sqrt{\frac{\hbar}{\mu\omega}}\left[\sqrt{\frac{n}{2}}\,\delta_{k,n-1} + \sqrt{\frac{n+1}{2}}\,\delta_{k,n+1}\right] \tag{5.36}$$

Using matrix notation and the rule that, if every element of a matrix is multiplied by the same number, this common factor can be taken out, the array (5.35) can be written:

$$(x) = \sqrt{\frac{\hbar}{2\mu\omega}}\begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdot \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \cdot \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdot \\ 0 & 0 & \sqrt{3} & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \tag{5.37}$$

Two features are remarkable: Most matrix elements of (5.37) vanish, and (5.37) is a real symmetric matrix. Of these properties the first is peculiar to the harmonic oscillator, whereas the second is an example of a very general property (see Chapter 8).

Exercise 5.4. Using Exercise 5.3 and (5.23) and (5.36), calculate the matrix elements of the momentum operator,

$$p_{nk} = \int_{-\infty}^{+\infty} \psi_n^* \frac{\hbar}{i}\frac{d\psi_k}{dx}\,dx$$

and compare the result with the matrix for x.

Substituting the result (5.36) into (5.33), we obtain

$$\langle x\rangle = \sqrt{\frac{\hbar}{2\mu\omega}}\sum_{n=1}^{\infty}\sqrt{n}(c_n^* c_{n-1}e^{i\omega t} + c_{n-1}^* c_n e^{-i\omega t}) \tag{5.38}$$

If we set

$$c_n = |c_n|e^{i\varphi_n}$$

we can write

$$\langle x\rangle = \sqrt{\frac{2}{\mu\omega^2}}\sum_{n=0}^{\infty}\sqrt{n\hbar\omega}\,|c_n|\,|c_{n-1}|\cos(\omega t + \varphi_{n-1} - \varphi_n) \tag{5.39}$$

This expression is exact.

Exercise 5.5. By using the results of Section 4.3 show directly that for the linear harmonic oscillator $\langle x \rangle$ satisfies the classical equation of motion

$$\frac{d^2\langle x \rangle}{dt^2} + \omega^2 \langle x \rangle = 0$$

Solve this equation and show that it leads to the general form of (5.39).

If $\varphi_{n-1} - \varphi_n = \alpha$ is independent of n, if $|c_{n-1}| \simeq |c_n|$, and if c_n is appreciably different from zero only for large n, so that $E_n \simeq n\hbar\omega$, then we have approximately

$$\langle x \rangle \simeq \sqrt{\frac{2}{\mu\omega^2}} \left(\sum_{n=0}^{\infty} \sqrt{E_n}\, |c_n|^2 \right) \cos(\omega t + \alpha) \tag{5.40}$$

Equation (5.40) bears a close resemblance to the classical equation for a harmonic oscillator. If E is the energy of a classical oscillator, its instantaneous position $x(t)$ is

$$x(t) = \sqrt{\frac{2E}{\mu\omega^2}} \cos(\omega t + \alpha) \tag{5.41}$$

We see that the quantum equation (5.40) will relate expectation values and, in the correspondence limit of large quantum numbers, go over into the classical equations (5.41), if we write

$$\langle \sqrt{E} \rangle = \sum_{n=0}^{\infty} \sqrt{E_n}\, |c_n|^2 \tag{5.42}$$

But this is precisely what is to be expected, if the only allowed definite energy values of a harmonic oscillator are the eigenvalues E_n, and if $|c_n|^2$ is the probability for the occurrence of E_n in the given state [see assumptions (a) and (b) above]. The expectation value of any function of the energy would be

$$\langle f(E) \rangle = \sum_{n=0}^{\infty} f(E_n)\, |c_n|^2 \tag{5.43}$$

and (5.42) is a special case of this for $f(E) = \sqrt{E}$.

Exercise 5.6. Calculate the expectation value of momentum $\langle p \rangle$ for a wave packet in a linear harmonic oscillator. Make approximations similar to those leading to (5.40), and compare again with the appropriate classical equation.

5. *The Double Oscillator. Preliminary Remarks.* So far we have discussed in this chapter the simple linear harmonic oscillator. Now we shall supplement this discussion by study of a more complicated potential, pieced together

from two harmonic oscillators. The discontinuities which arise in the shape of this potential will lead to a consideration of the question of boundary conditions whose general importance transcends the special example which we have chosen to illustrate them.

The example comes from molecular physics. There we frequently encounter motion in the neighborhood of a stable equilibrium configuration, approximated by a harmonic potential. To be sure, one-dimensional models are of limited utility. Even diatomic molecules rotate in space, besides vibrating along a straight line. Nevertheless, important qualitative features can be exhibited with a linear model, and some quantitative estimates can also be obtained.

Let us consider, as a model, two masses μ_1 and μ_2, constrained to move in a straight line and connected with each other by a spring whose force constant is k and whose length at equilibrium is a. If x_1 and x_2 are the coordinates of the two mass points, and p_1 and p_2 their momenta, it is shown in classical mechanics that the nonrelativistic two-body problem can be separated into the trivial motion of the center of mass and an equivalent one-body motion, executed by a particle of mass $\mu = \mu_1\mu_2/(\mu_1 + \mu_2)$ with a coordinate $x = x_1 - x_2$ about a fixed center under the action of the elastic force. Only the relative motion of the reduced mass μ will be considered in this chapter.[7]

The wave equation corresponding to the equivalent one-body problem is

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi(x, t)}{\partial x^2} + \tfrac{1}{2}k(|x| - a)^2\psi(x, t) \tag{5.44}$$

If $a = 0$, (5.44) reduces to the wave equation for the simple linear harmonic oscillator. If $a \neq 0$, it is almost the equation of a harmonic oscillator whose equilibrium position is shifted by an amount a, but it is not quite that. For it is important to note that the *absolute value* of x appears in the potential energy $V = \frac{1}{2}k(|x| - a)^2$, if Hooke's law is assumed to hold for all values of the interparticle coordinate x. As shown in Figure 5.2, we have two parabolic potentials, one when particle 1 is to the right of particle 2 ($x > 0$), the other when the particles are in reverse order ($x < 0$). The parabolas are joined at $x = 0$ with the common value $V(0) = V_0 = \frac{1}{2}ka^2$. Classically, if $E < V_0$, we can assume that only one of these potential wells is present, for no penetration of barrier is possible. In quantum mechanics, even if $E < V_0$ the wave function may have a finite value at $x = 0$, which measures the

[7] The separation of the relative motion from the motion of the center of mass will be effected in Section 15.5. If the forces between two bodies are equal in magnitude and opposite in direction, classically the relative motion can be replaced by an equivalent one-body motion of the reduced mass. The correspondence principle suggests that these general dynamical features survive the transition to quantum mechanics.

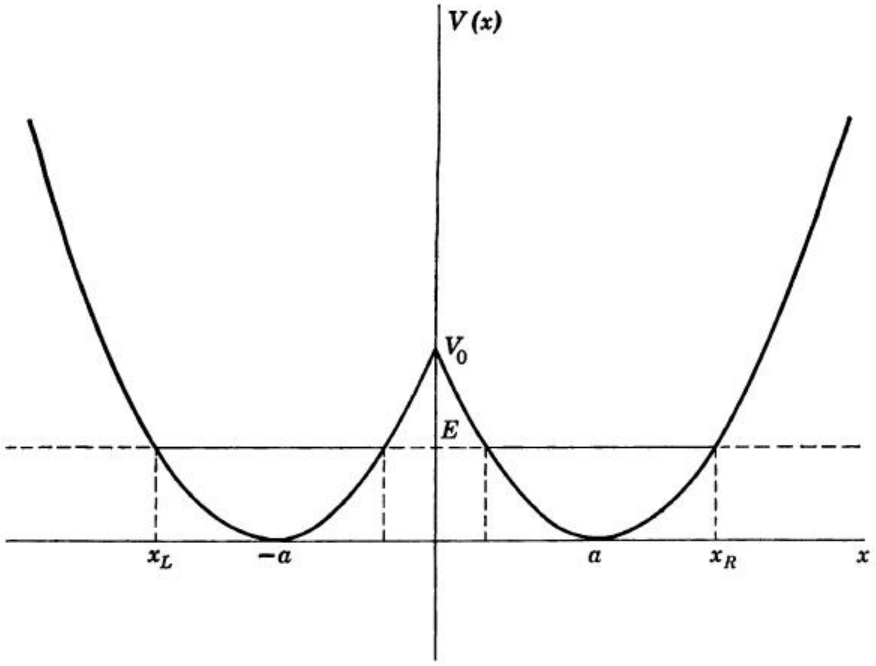


Figure 5.2. $V(x)$ for a double oscillator. x_L and x_R are the external classical turning points. If $E < V_0$, there are also two internal turning points, but the tunnel effect permits penetration of the barrier.

probability that the two particles are found in the same place; hence, the barrier can be penetrated.

The Schrödinger equation corresponding to (5.44) is

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \tfrac{1}{2}(k\,|x| - a)^2\psi(x) = E\psi(x) \tag{5.45}$$

This equation must be supplemented by boundary conditions at $x \to \pm\infty$. For $|x| \gg a$, (5.45) approaches the Schrödinger equation (5.3) for the simple harmonic oscillator; hence, the considerations of Section 5.2 may be applied, and the physically acceptable eigenfunctions must be required to vanish as $|x| \to \infty$.

Before attempting to solve (5.45), we note that as the parameter a is varied from 0 to ∞, the potential changes from the limit (I) of a single harmonic oscillator well to the other limit (II) of two separate oscillator wells, divided by an infinitely high and broad potential wall. In case I we have nondegenerate energy eigenvalues

$$E_n = \hbar\omega(n + \tfrac{1}{2}) = \hbar\sqrt{\frac{k}{\mu}}(n + \tfrac{1}{2}) \qquad (n = 0, 1, 2 \cdots) \tag{5.46}$$

In case II the energy values are the same as given by (5.46), but each is doubly degenerate, since the system may occupy an eigenstate of either the

harmonic oscillator well on the left or the one on the right. As a is varied, energies and eigenfunctions must change continuously from limiting case I to limiting case II. It is customary to call this kind of continuous change of an external parameter an *adiabatic* change of the system. It is useful to note that as the potential is being distorted continuously certain features of the eigenfunctions remain unaltered. Such features are known as *adiabatic invariants.*

An example is provided by the number of zeros, or nodes, of the eigenfunctions. If an eigenfunction has n nodes, as the eigenfunction of potential I belonging to the eigenvalue E_n does, this number cannot change in the course of the transition to II. We prove this assertion in two steps:

(a) No two adjacent nodes disappear by coalescing as a changes, nor can new nodes ever be created by the inverse process. If two nodes did coalesce at $x = x_0$, the extremum of ψ between them would also have to coincide with the nodes. Hence, both ψ and its first derivative ψ' would vanish at this point. By the differential equation (5.45) this would imply that ψ'', ψ''', and all higher derivatives also vanish at this point. But a function all of whose derivatives vanish can only be $\psi \equiv 0$.[8]

(b) No node can wander off to or in from infinity as a changes. To show this we only need to prove that all nodes are confined to the region between the two extreme classical turning points of the motion, i.e., the region between x_L and x_R in Figure 5.2. Classically, the coordinate of a particle with energy E is restricted by $x_L \leqslant x \leqslant x_R$, where x_L and x_R are the smallest and largest roots respectively of $V(x) = E$. From Schrödinger's equation we infer

$$\int_{-\infty}^{x} \psi^*(x')[E - V(x')]\psi(x')\,dx' = -\frac{\hbar^2}{2\mu}\left(\left|\psi^*(x')\psi'(x')\right|_{-\infty}^{x} - \int_{-\infty}^{x} |\psi'(x')|^2\,dx'\right) \tag{5.47}$$

Let $x \leqslant x_L$. Then the integral on the left is negative definite, hence

$$\psi^*(x)\psi'(x) > 0 \quad \text{if } x \leqslant x_L \tag{5.48}$$

Equation (5.48) holds similarly if $x \geqslant x_R$. It follows that outside the classical region there can be no node and no extremum. This can also be seen directly from the Schrödinger equation, since ψ''/ψ is positive outside the classical region (see Figure 6.4).

Being an adiabatic invariant, the number of nodes n characterizes the eigenfunctions of the double oscillator for any value of a. Figure 5.3 shows

[8] It will be shown in Section 5.6 that ψ and ψ' must be continuous. Hence, the presence of isolated singularities in V (as at $x = 0$ for the double oscillator) does not affect this conclusion.

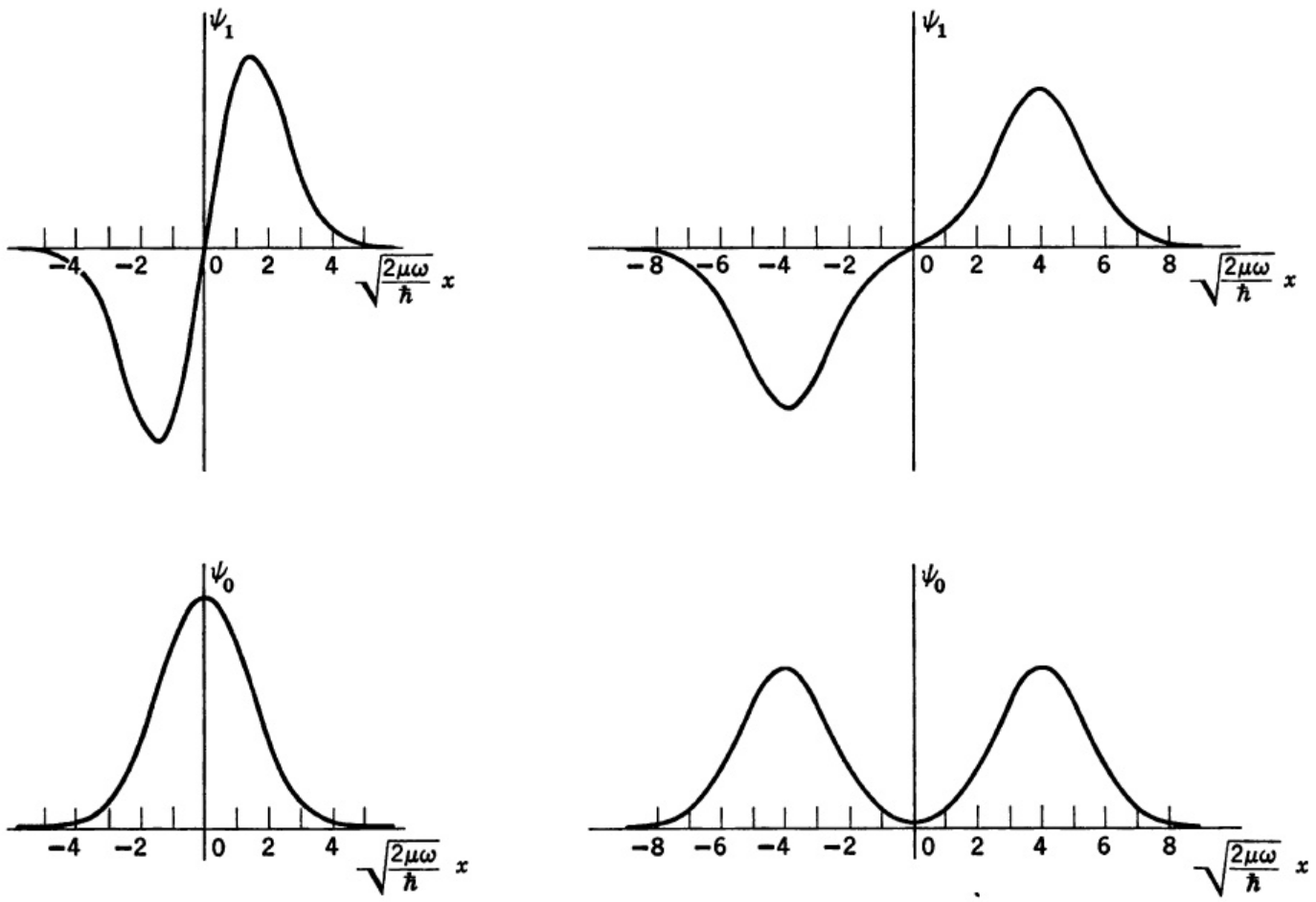


Figure 5.3. The two lowest energy eigenfunctions ψ_0 and ψ_1. In case I ($a = 0$) we have a simple harmonic oscillator, no barrier, and $E_1 - E_0 = \hbar\omega$. In case II ($\sqrt{2\mu\omega/\hbar}\, a = 4$) the double oscillator has a high barrier, and $E_1 - E_0 \approx 10^{-3}\hbar\omega$. The number of nodes characterizes the eigenfunctions.

this for the two lowest energy eigenvalues ($n = 0, 1$). Notice also that the eigenfunctions maintain their parity as a varies, since (5.45), owing to the presence of $|x|$ in the potential energy, is invariant under reflection.

The two eigenfunctions ψ_0 and ψ_1 correspond to $E = \frac{1}{2}\hbar\omega$ and $\frac{3}{2}\hbar\omega$ if $a = 0$ (case I). For $a \to \infty$ (case II) they become degenerate with the common energy $\frac{1}{2}\hbar\omega$. When a is very large, the linear combinations $\psi_0 + \psi_1$ and $\psi_0 - \psi_1$ are *approximate* eigenfunctions corresponding to the wave function being concentrated at $x = +a$ and at $x = -a$ respectively.

6. *The Double Oscillator. Eigenvalues and Eigenfunctions.* The rigorous solution of (5.45) is facilitated by introducing for positive x

$$z = \left(\frac{4\mu k}{\hbar^2}\right)^{1/4}(x - a) = \left(\frac{2\mu\omega}{\hbar}\right)^{1/2}(x - a) \qquad (x > 0)$$

and

$$E = \hbar\omega(\nu + \tfrac{1}{2}) \tag{5.49}$$

We obtain for positive x the differential equation

$$\frac{d^2\psi}{dz^2} + \left(\nu + \frac{1}{2} - \frac{z^2}{4}\right)\psi = 0 \tag{5.50}$$

For negative x the same equation is obtained except that now the substitution

$$z' = \left(\frac{2\mu\omega}{\hbar}\right)^{1/2}(x + a) \qquad (x < 0)$$

must be used. The differential equation valid for negative x is

$$\frac{d^2\psi}{dz'^2} + \left(\nu + \frac{1}{2} - \frac{z'^2}{4}\right)\psi = 0 \tag{5.51}$$

which has the same form as (5.50). For $a = 0$, the case of the simple linear harmonic oscillator, $z' = z$, and the two equations become identical. The boundary condition $\psi \to 0$ as $x \to \pm\infty$ implies that we must seek solutions of (5.50) and (5.51) which vanish as $z \to +\infty$ and $z' \to -\infty$.

Instead of proceeding to a detailed power series treatment of this differential equation, we refer to a standard treatise on mathematical analysis[2] for the solutions of (5.50). The particular solution of (5.50) which vanishes for very large positive values of z is called a *parabolic cylinder function*. It is denoted by $D_\nu(z)$ and defined as

$$D_\nu(z) = 2^{\nu/2}e^{-(z^2/4)}\left[\frac{\Gamma(\frac{1}{2})}{\Gamma[(1-\nu)/2]}\,{}_1F_1\left(-\frac{\nu}{2};\frac{1}{2};\frac{z^2}{2}\right)\right.$$
$$\left. + \frac{z}{\sqrt{2}}\frac{\Gamma(-\frac{1}{2})}{\Gamma(-\nu/2)}\,{}_1F_1\left(\frac{1-\nu}{2};\frac{3}{2};\frac{z^2}{2}\right)\right] \tag{5.52}$$

${}_1F_1$ is the *confluent hypergeometric* (or Kummer) *function.* Its power series expansion is

$$ {}_1F_1(a; c; z) = 1 + \frac{a}{c}\frac{z}{1!} + \frac{a(a+1)}{c(c+1)}\frac{z^2}{2!} + \cdots \tag{5.53} $$

If z is large and *positive* ($z \gg 1$ and $z \gg |\nu|$),

$$ D_\nu(z) \sim e^{-(z^2/4)} z^\nu \left[1 - \frac{\nu(\nu-1)}{2z^2} + \frac{\nu(\nu-1)(\nu-2)(\nu-3)}{2 \cdot 4 \cdot z^4} \pm \cdots \right] \tag{5.54} $$

and if z is large and *negative* ($z \ll -1$ and $z \ll -|\nu|$),

$$ \begin{aligned} D_\nu(z) \sim{}& e^{-(z^2/4)} z^\nu \left[1 - \frac{\nu(\nu-1)}{2z^2} \pm \cdots \right] \\ & - \frac{\sqrt{2\pi}}{\Gamma(-\nu)} e^{\nu\pi i} e^{z^2/4} z^{-\nu-1} \left[1 + \frac{(\nu+1)(\nu+2)}{2z^2} + \cdots \right] \end{aligned} \tag{5.55} $$

Although the series in the brackets all diverge for any finite value of z, (5.54) and (5.55) are useful *asymptotic* expansions of $D_\nu(z)$.

Exercise 5.7. Using the identity

$$ \Gamma(1+\nu)\Gamma(-\nu) = -\frac{\pi}{\sin \nu\pi} \tag{5.56} $$

obtain the eigenvalues of the simple harmonic oscillator from (5.55). Show the connection between the parabolic cylinder functions (5.52) and the eigenfunctions (5.12).

If $D_\nu(z)$ is a solution of (5.50), $D_\nu(-z)$ is also a solution of the same equation, and these two solutions are linearly independent unless ν is a nonnegative integer. Inspection of the asymptotic behavior shows that the particular solution of (5.51) which vanishes for very large negative values of z' must be $D_\nu(-z')$.

It follows that a double oscillator eigenfunction must be proportional to $D_\nu(z)$ for positive values of x, and proportional to $D_\nu(-z')$ for negative values of x. It remains to join these two solutions at $x = 0$, the point where the two parabolic potentials meet with discontinuous slope. This problem leads to a re-examination of the Schrödinger equation if the potential is nonanalytic at an isolated point x_0. We assume that such a singular potential function can be approximated by a regular one; the former can be regarded as the limiting case of the latter. Since the Schrödinger equation is a second-order differential equation, ψ and its first derivative must be continuous everywhere. Alternatively, if $x = x_0$ is the point of singularity, we get by

integrating the Schrödinger equation from $x = x_0 - \varepsilon$ to $x = x_0 + \varepsilon$:

$$\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon) = \int_{x_0-\varepsilon}^{x_0+\varepsilon} \frac{2\mu}{\hbar^2} [V(x) - E]\psi(x)\, dx$$

As long as $V(x)$ is finite, whether analytic or not, this equation implies that ψ' is continuous across the singularity. Hence, ψ itself must also be continuous.

Thus the joining condition to be assumed at a singular point of the potential, if V has a finite value, is that the wave function and its slope must be matched continuously. The probability current density, which is made up of ψ and ψ', must also be continuous—an evident physical requirement, if there are no sources and sinks of probability, i.e., of particles.

Armed with this knowledge we return to the double oscillator. Since it is invariant under reflection ($x \to -x$), the eigenfunctions can be assumed to have definite parity, even or odd. If an even function of x has a continuous slope at $x = 0$, as the joining condition requires, that slope must be zero. On the other hand, if an odd function of x is continuous at the origin, it must vanish there. Matching ψ and ψ' at $x = 0$ thus leads to

$$D_\nu'\left(-\sqrt{\frac{2\mu\omega}{\hbar}}\, a\right) = 0 \tag{5.57}$$

for even ψ, and

$$D_\nu\left(-\sqrt{\frac{2\mu\omega}{\hbar}}\, a\right) = 0 \tag{5.58}$$

for odd ψ. These are transcendental equations for ν.

Exercise 5.8. Show that if $a = 0$, the roots of (5.57) and (5.58) give the eigenvalues of the simple harmonic oscillator.

In general, it is difficult to calculate the roots ν of (5.57) and (5.58). Figure 5.4 shows how the lowest eigenvalues depend on the parameter $\sqrt{2\mu\omega/\hbar}\, a$. A few of the corresponding eigenfunctions are plotted in Figure 5.3. The unnormalized eigenfunctions are

$$\psi(x) = \begin{cases} D_\nu\left(\sqrt{\dfrac{2\mu\omega}{\hbar}}\,(x - a)\right) & (x \geqslant 0) \\ \pm D_\nu\left(-\sqrt{\dfrac{2\mu\omega}{\hbar}}\,(x + a)\right) & (x \leqslant 0) \end{cases} \tag{5.59}$$

where the upper (lower) sign is to be used if ν is a root of (5.57) [(5.58)].

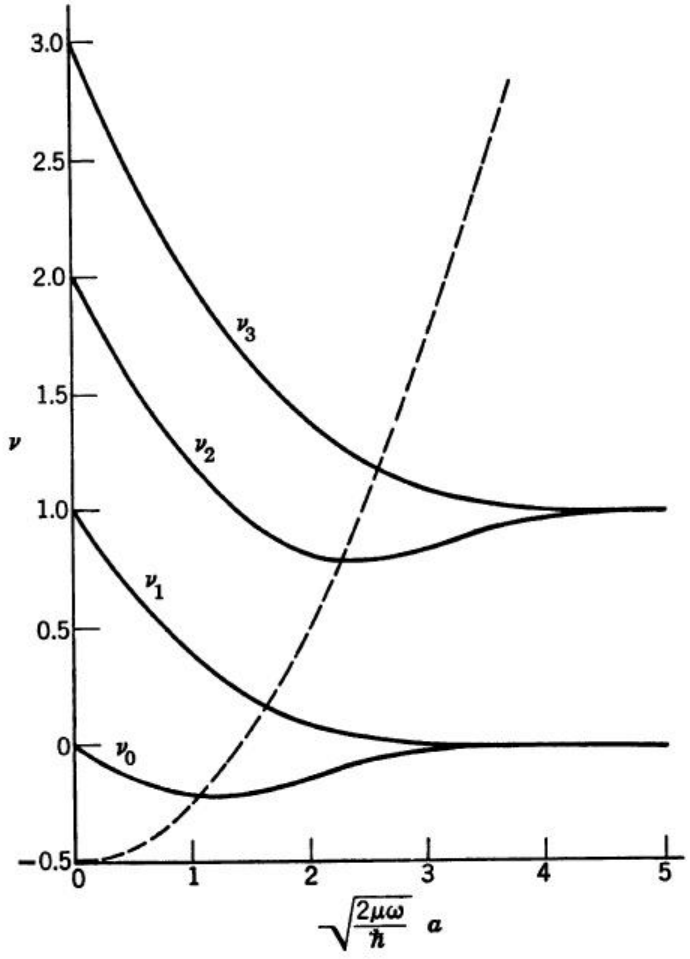


Figure 5.4. $\nu = (E/\hbar\omega) - \frac{1}{2}$ versus $\sqrt{2\mu\omega/\hbar}\,a$ for the four lowest eigenstates of the double oscillator. The dashed curve shows $(V_0/\hbar\omega) - \frac{1}{2}$ for a comparison of the energy levels with the barrier height.

Explicit approximate formulas for the eigenvalues can be given if $V_0 \gg E$ and

$$\sqrt{\frac{2\mu\omega}{\hbar}}\,a \gg 1 \qquad \text{or} \qquad V_0 = \tfrac{1}{2}\mu a^2\omega^2 \gg \tfrac{1}{4}\hbar\omega$$

These conditions represent the case of two almost completely separated oscillator wells, important in applications to molecules. For simplicity we shall only work out an approximation to the two roots which lie near $\nu = 0$, i.e., the lowest two energy eigenvalues. As $a \to \infty$, they become degenerate and equal to $\frac{1}{2}\hbar\omega$.

For the odd case we obtain from (5.55) with $z = -\sqrt{2\mu\omega/\hbar}\,a$ to first

approximation ($\nu \approx 0$)

$$\nu_{\text{odd}} = \sqrt{\frac{\mu\omega}{\hbar\pi}}\, a \exp\left(-\frac{2V_0}{\hbar\omega}\right) = \sqrt{\frac{2V_0}{\hbar\omega\pi}} \exp\left(-\frac{2V_0}{\hbar\omega}\right) \tag{5.60}$$

Exercise 5.9. Prove this result, noting that, if $\nu \approx 0$, $\Gamma(-\nu) \approx -1/\nu$.

For z negative, $|z| \gg 1$, and $\nu \approx 0$ we have

$$D_\nu'(z) \approx -\frac{z}{2}\exp\left(-\frac{z^2}{4}\right) + \sqrt{2\pi}\,\frac{\nu}{2}\exp\left(\frac{z^2}{4}\right)$$

from which it follows that for $\nu \approx 0$, $\nu_{\text{even}} \approx -\nu_{\text{odd}}$. The splitting of the two lowest energy levels is therefore

$$\Delta E = \hbar\omega(\nu_{\text{odd}} - \nu_{\text{even}}) = 2\hbar\omega\sqrt{\frac{2V_0}{\hbar\omega\pi}} \exp\left(-\frac{2V_0}{\hbar\omega}\right)$$

The frequency corresponding to this energy splitting is

$$\omega' = \frac{\Delta E}{\hbar} = 2\omega\sqrt{\frac{2V_0}{\hbar\omega\pi}} \exp\left(-\frac{2V_0}{\hbar\omega}\right) \tag{5.61}$$

The physical significance of this frequency is best appreciated if we consider a system which is initially represented by a wave function proportional to $\psi_0 + \psi_1$, a wave function with a single peak around $x = +a$. If $x = x_1 - x_2$ is the coordinate difference for two elastically bound particles, as described in Section 5.5, this initial condition implies that at $t = 0$ particle 1 is definitely to the right of particle 2. What is the time development of this system? Neglecting questions of normalization, we have

$$\begin{aligned}
\psi(x, t) &= \exp\left(-\frac{i}{\hbar}E_0 t\right)\psi_0 + \exp\left(-\frac{i}{\hbar}E_1 t\right)\psi_1 \\
&= \tfrac{1}{2}\exp\left(-\frac{i}{\hbar}E_0 t\right)\{(\psi_0 + \psi_1)[1 + \exp(-i\omega' t)] \\
&\quad + (\psi_0 - \psi_1)[1 - \exp(-i\omega' t)]\} \\
&= \exp\left[-\frac{i(E_0 + E_1)}{2\hbar}t\right]\left[(\psi_0 + \psi_1)\cos\frac{\omega'}{2}t + i(\psi_0 - \psi_1)\sin\frac{\omega'}{2}t\right]
\end{aligned} \tag{5.62}$$

This last form shows clearly that the system shuttles back and forth between $\psi_0 + \psi_1$ and $\psi_0 - \psi_1$ with the frequency $\omega'/2$. It takes a time $\tau = \pi/\omega'$ for the system to change from its initial state $\psi_0 + \psi_1$ to the state $\psi_0 - \psi_1$, which means that the particles have exchanged their places in an entirely unclassical fashion, and the wave function is now peaked around $x = -a$.

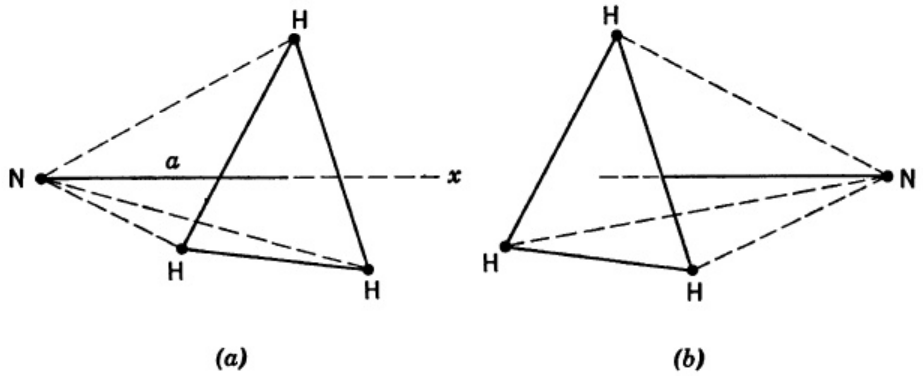


Figure 5.5. The ammonia (NH_3) molecule. The inversion spectrum arises from the motion of the nitrogen atom along the line perpendicular to the plane of the hydrogen atoms. A potential barrier prevents classical oscillations between equilibrium configurations (*a*) and (*b*), but quantal barrier penetration can produce strong oscillations.

Since E was assumed to be much less than V_0, this exchange requires that the system tunnel with frequency $\omega'/2$ through the classically inaccessible barrier region indicated in Figure 5.2. The ratio of the time τ during which the exchange takes place to the period of the harmonic oscillator is given approximately by

$$\frac{\omega\tau}{2\pi} = \frac{\omega}{2\omega'} = \frac{1}{4}\sqrt{\frac{\hbar\omega\pi}{2V_0}}\exp\left(\frac{2V_0}{\hbar\omega}\right) \tag{5.63}$$

If the barrier V_0 is high compared to $\hbar\omega$, the tunneling is strongly inhibited by the presence of the exponential factor.

A numerical example from molecular physics will serve as an illustration. Let the equilibrium distance of the particles in a molecule be $a = 10^{-8}$ cm, and the reduced mass $\mu = 10^{-23}$ gram. For $\omega = 2 \times 10^{15}\ \text{sec}^{-1}$ (corresponding to an infrared vibration spectrum common in many molecules) we have $V_0/\hbar\omega \simeq 10^3$. τ turns out to be superastronomical (about 10^{400} years); hence the exchange "hardly ever" takes place. On the other hand, if $\omega = 10^{12}\ \text{sec}^{-1}$, corresponding to microwave vibrations of 0.2 cm wavelength, the value of ω' obtained from Figure 5.4 is approximately $8 \times 10^{11}\ \text{sec}^{-1}$, which is again in the microwave region.

The ammonia (NH_3) molecule is an example of a system in which transitions between the two states ψ_0 and ψ_1 can be induced by microwave radiation of frequency ω'.[9] There are two stable equilibrium positions of the nitrogen atom in the NH_3 molecule, symmetric with respect to the plane of the hydrogen atoms (Figure 5.5). One important vibrational mode consists of

[9] For this and other interesting applications of quantum mechanics to microwave spectroscopy see C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill Book Co., New York, 1955.

oscillations of the nitrogen atom along the axis of the pyramid. If a is the distance from the equilibrium position to the symmetry plane, and x the instantaneous coordinate of the nitrogen atom on the axis, the potential energy will resemble Figure 5.2 closely, and our simple one-dimensional double oscillator model may be applied. The barrier which inhibits the inversion of the ammonia molecule from configuration a to b causes splitting of the vibration levels. Transitions between the split components give rise to a strong spectral line in the microwave region (*inversion spectrum*). Since the effect depends on quantum mechanical tunneling, we may well count the successful description of the inversion spectrum among the impressive accomplishments of quantum mechanics.

The double oscillator also provides a primitive model of a diatomic molecule. The force by which two similar atoms, such as two hydrogen atoms, are bound together in a diatomic molecule has its origin in the fact that an electron, which is classically confined to the vicinity of one or the other of the two nuclei, can be exchanged between them by quantal tunneling and is therefore shared by the two atoms.

We can get a qualitative understanding of this binding if we consider an electron in the field of two identical one-dimensional wells whose centers (the nuclei) are separated by a fixed distance X. For the example of the double oscillator potential of Figure 5.2 the dependence of the energy $E_e^{(i)}$ of each electronic eigenstate i on the interatomic distance $X = 2a$ can be inferred from Figure 5.4. If the nuclei were really fixed in their positions, the force between them would be $F^{(i)} = -[\partial E_e^{(i)}/\partial X]$. The quasi-static approximation which underlies the theory of molecular motion is based on the assumption that the nuclei move so slowly compared with the electrons that the force between the atoms can still be calculated by differentiation of the energies $E_e^{(i)}$. The function $E_e^{(i)}(X)$ thus serves as the potential energy for the motion of the nuclei if the electrons are in state i. Since X is regarded as an external parameter which changes slowly, allowing the electrons to remain in a quasi-stationary state throughout, the approximation is said to be *adiabatic*.

If μ_n is the reduced mass of the "homonuclear diatomic molecule," X the relative coordinate of the two "nuclei," μ the mass of the electron, and x its coordinate relative to the center of mass, the Schrödinger equation for our example may be written as

$$\left[-\frac{\hbar^2}{2\mu_n}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}\mu\omega^2\left(|x| - \frac{X}{2}\right)^2\right]\psi(x, X) = E\psi(x, X) \qquad (5.64)$$

provided that the center of mass of the molecule is assumed to be at rest. We also assume that $X > 0$ and thus neglect the possibility of inversion of the

molecule which was discussed above. For a real molecule, a repulsive interaction $V(X)$ between the nuclei must be included in (5.64).

The adiabatic approximation[10] consists of assuming that the solution has the form

$$\psi(x, X) = \varphi_X^{(i)}(x)\eta(X) \tag{5.65}$$

so that the Schrödinger equation separates into a stationary state equation for the electron:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}\mu\omega^2\left(|x| - \frac{X}{2}\right)^2\right]\varphi_X^{(i)}(x) = E_e^{(i)}(X)\varphi_X^{(i)}(x) \tag{5.66}$$

corresponding to a fixed value of X, and a second equation describing the motion of the nuclei:

$$\left[-\frac{\hbar^2}{2\mu_n}\frac{\partial^2}{\partial X^2} + E_e^{(i)}(X)\right]\eta(X) = E\eta(X) \tag{5.67}$$

By substituting the product wave function (5.65) in the Schrödinger equation (5.64), we see that (5.66) and (5.67) result, if we can neglect the terms

$$-\frac{\hbar^2}{\mu_n}\frac{\partial\varphi}{\partial X}\frac{\partial\eta}{\partial X} - \frac{\hbar^2}{2\mu_n}\frac{\partial^2\varphi}{\partial X^2}\eta \tag{5.68}$$

We shall estimate their magnitude presently.

By inspection of Figure 5.4 we see that the molecule can vibrate about a stable equilibrium configuration only if the electron is in one of the *symmetric* eigenstates. Confining ourselves to the electronic *ground* state ($i = 0$) we see that near the minimum of $E_e^{(0)}$ at $X = X_0$ we may write approximately

$$E_e^{(0)}(X) = E^0 + \tfrac{1}{2}\mu\omega^2 C(X - X_0)^2 \tag{5.69}$$

where C is a number of the order of unity. It follows that the nuclei perform harmonic oscillations with frequency $\simeq\sqrt{\mu/\mu_n}\,\omega$. Since actual molecules move in three dimensions and can rotate besides vibrating along the line joining the nuclei, their spectra exhibit more complex features, but the general nature of the approximations used is the same.

The accuracy of the adiabatic approximation is measured by the relative importance of the terms (5.68) compared with the kinetic energy $p_n^2/2\mu_n$ of the molecule. The first, and larger, of the two terms is of the order of magnitude $p_n p_e/2\mu_n$, since the wave function $\varphi_X^{(i)}(x)$ is equally sensitive to changes in X as in $2x$ so that

$$\left|\frac{\partial\varphi}{\partial X}\right| \simeq \frac{1}{2}\left|\frac{\partial\varphi}{\partial x}\right|$$

[10] The term *adiabatic approximation* applies to a general method. This particular form of it is referred to as the *Born-Oppenheimer approximation*.

As a necessary condition for the validity of the adiabatic approximation we thus obtain

$$\frac{p_n^2}{2\mu_n} \gg \frac{p_n p_e}{2\mu_n} \qquad \text{or} \qquad p_n \gg p_e$$

As estimates for the momenta we have (Problem 2)

$$p_e \simeq \sqrt{\mu\hbar\omega/2} \qquad \text{and} \qquad p_n \simeq \sqrt{\mu_n\hbar\sqrt{\mu/\mu_n}\omega/2}$$

Hence, the approximation may be expected to be good if

$$\left(\frac{\mu}{\mu_n}\right)^{1/4} \ll 1$$

which is reasonably well satisfied for molecules.

Problems

1. Calculate the matrix elements of x^2 with respect to the eigenfunctions of the harmonic oscillator and write down the first few rows and columns of the matrix. Can the same result be obtained directly by matrix algebra from a knowledge of the matrix elements of x?
2. Calculate the expectation values of the potential and kinetic energies in any stationary state of the harmonic oscillator. (See also Exercise 8.19.)
3. In first approximation, calculate the change in the energy levels of a linear harmonic oscillator that is perturbed by a potential gx^4.
4. Calculate the probability that the coordinate of a linear harmonic oscillator in its ground state has a value greater than the amplitude of a classical oscillator of the same energy.
5. Prove that

$$H_n(\xi) = \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{+\infty} (\xi + iu)^n e^{-u^2}\, du$$

   is an integral representation for Hermite polynomials.
6. Show that if an ensemble of linear harmonic oscillators is in thermal equilibrium, governed by the Boltzmann distribution, the probability per unit length of finding a particle with displacement x is a Gaussian distribution. Plot the width of the distribution as a function of temperature. Check the results in the classical and the low temperature limits. (*Hint*. The formula in Problem 5 may be used.)
7. Show that as inadequate a variational trial function as

$$\psi(x) = \begin{cases} C\left(1 - \dfrac{|x|}{a}\right) & \text{for } |x| \leqslant a \\ 0 & \text{for } |x| > a \end{cases}$$

   yields, for the optimum value of a, an upper limit to the ground state energy of the linear harmonic oscillator, which lies within less than 10 percent of the exact value.

8. Work out an approximation to the energy splitting between the second and third excited levels of the double oscillator, assuming the distance between the wells to be very large compared with the classical amplitude of the zero-point vibrations.

9. Apply the variational method to the double oscillator, using a real trial wave function of the form

$$\psi(x) = \alpha\psi_n(x - a) + \beta\psi_n(x + a)$$

where $\psi_n(x)$ denotes an eigenfunction of the simple linear harmonic oscillator. Show that the energy eigenvalues are approximated by[11]

$$\langle H \rangle = \frac{A_n \pm B_n}{1 \pm C_n}$$

where

$$A_n = \int \psi_n(x - a)H\psi_n(x - a)\,dx = \int \psi_n(x + a)H\psi_n(x + a)\,dx$$

$$B_n = \int \psi_n(x - a)H\psi_n(x + a)\,dx = \int \psi_n(x + a)H\psi_n(x - a)\,dx$$

and C_n is the *overlap integral*

$$C_n = \int \psi_n(x + a)\psi_n(x - a)\,dx$$

Calculate to a first approximation the splitting of the oscillator ground state for very large but finite values of a, and verify the result (5.61).

[11] The approximation method employed in this problem illustrates some of the techniques which are commonly used in the quantum theory of the chemical bond and parallels especially the theory of the positive H_2 ion. See C. A. Coulson, *Valence*, Clarendon Press, Oxford, 1952. Also, F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill Book Company, New York, 1968, and R. G. Parr, *Quantum Theory of Molecular Electronic Structure*, W. A. Benjamin, New York, 1963.

CHAPTER 6

Piecewise Constant Potentials in One Dimension

1. ***Introduction.*** Of all Schrödinger equations the one for a constant potential is mathematically the simplest. We know from Chapter 2 that the solutions are harmonic *plane waves*, with wave number

$$k = \sqrt{2\mu(E - V)}/\hbar$$

The reason for resuming the study of the Schrödinger equation with such a potential is that the qualitative features of a real physical potential can often be approximated reasonably well by a potential which is pieced together from a number of constant portions. For instance, although the forces acting between a proton and a neutron are not accurately known on theoretical grounds, it is known that, unlike the electrostatic forces which hold an atom together, the nuclear forces have a short range: they extend to some distance, and then drop to zero very fast. Figure 6.1 shows what these forces might look like and also how a rectangular potential well approximates them.

A potential with the shape shown in Figure 6.1 is frequently called a *square well.* The one-dimensional potential of this form simulates the more realistic three-dimensional potential square well which is a central potential with $V = 0$ for $r > a$ and $V = -V_0$ for $r < a$.

There are many other cases in which such a schematic potential approximates the real situation sufficiently to provide an orientation at the expense of comparatively little mathematical work. In solid state physics a periodic potential, as shown in Figure 6.2, exhibits some of the important features of any periodic potential seen by an electron in a crystal lattice.

Quite generally, the piecewise constant potential in one dimension offers an instructive example, and the behavior of a particle subject to such a potential is well worth studying in some detail.

$V(x) =$ const. for all x is the trivial case of the free particle. We recapitulate it here briefly. The Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2\mu(E - V)}{\hbar^2}\psi = 0 \tag{6.1}$$

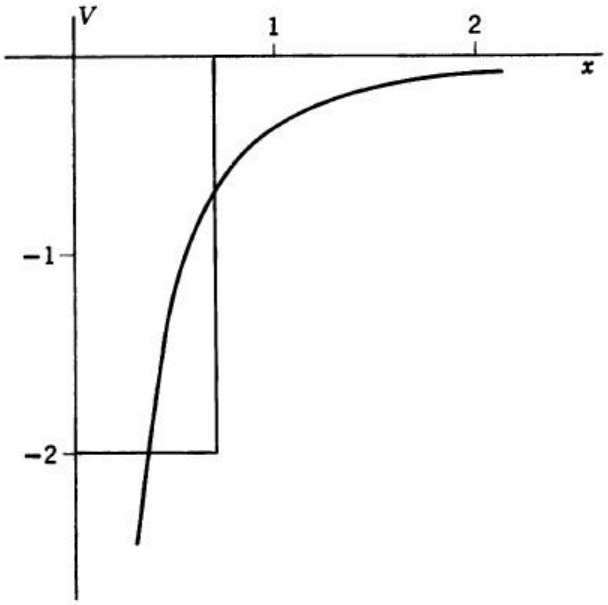


Figure 6.1. Possible shape of the potential representing the attractive part of the nuclear forces ($V = -e^{-x}/x$) and a square well approximating it.

If we write $p = \sqrt{2\mu(E - V)} = \hbar k$, the general solution of (6.1) is

$$\psi = Ae^{ikx} + Be^{-ikx} \tag{6.2}$$

For a solution to be physically useful k must not have any imaginary part. For if it did, ψ would grow beyond all bounds in the direction of either positive or negative x, or both. Hence, k must be real, but any real number will do. $E - V$ must be positive or zero, and the Schrödinger equation of the free particle has thus a *continuous* spectrum of eigenvalues, $E \geqslant V$. This means, of course, merely that the kinetic energy of a free particle must be positive definite. The totality of the solutions e^{ikx} and e^{-ikx}, where k can be any nonnegative number, is complete in the sense that any physically suitable wave packet can be expanded in terms of these eigenfunctions. This (Fourier) expansion theorem was the content of (2.12) and (2.13).

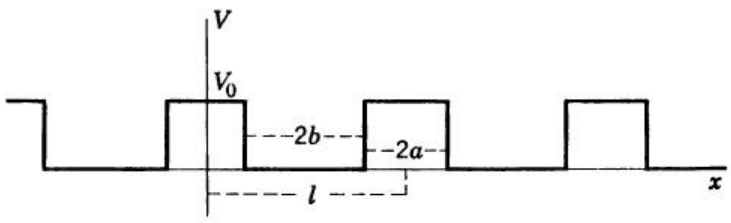


Figure 6.2. A periodic potential with rectangular sections (Kronig-Penney). The period has length $l = 2a + 2b$.

The eigenfunctions (6.2) are not quadratically integrable over all space. It is therefore impossible to speak of absolute probabilities and of expectation values for physical quantities in such a state. One way of avoiding this predicament would be to recognize the fact that physically no particle is ever absolutely free and that there is inevitably some confinement, the enclosure being for instance the wall of an accelerator tube or of the laboratory. V rises to infinity at the boundaries of the enclosure and does then not have the same value everywhere, the eigenfunctions are no longer infinite plane waves, and the eigenvalue spectrum is discrete rather than continuous (see Section 6.8). However, if the enclosure is very large compared with the de Broglie wavelength, the infinite plane wave is a useful idealization and an excellent approximation, and we shall gladly pay the price for using it.

Since normalization of $\int \psi^* \psi \, d\tau$ to unity is out of the question for infinite plane waves, we must decide on an alternative normalization for these wave functions.[1] A convenient tool in the discussion of such wave functions is the *delta function*.[2]

2. *The Delta Function.* The paradoxical feature of the delta function is that it is not a function at all. Rather, it is a symbol, $\delta(x)$, which for certain clearly defined purposes can be treated as if it were a function.

The delta function is a generalization of the Kronecker delta to the case of a continuous variable. The Kronecker delta δ_{ij} is defined for the discrete variables i and j as

$$\delta_{ij} = 0 \quad \text{if } i \neq j, \qquad \delta_{ii} = 1$$

Alternatively, it may be defined by

$$f(j) = \sum_{i=1}^{\infty} \delta_{ij} f(i) \tag{6.3}$$

if i and j take on the discrete values $1, 2, 3 \cdots$.

In generalization of (6.3) the delta function is defined by the equation

$$f(x') = \int_{-\infty}^{+\infty} \delta(x, x') f(x) \, dx \tag{6.4}$$

where $f(x)$ is an arbitrary well-behaved function. Since $f(x)$ can be changed "almost anywhere" without affecting the value $f(x')$, it is clear that $\delta(x, x') = 0$ everywhere except when x is very close to x'. Owing to the definition (6.4),

[1] It is possible to normalize the eigenfunctions (6.2) by imposing periodic boundary conditions. This will be discussed in Section 6.3.

[2] Also known as the *Dirac delta function*. A useful compendium of the properties of the delta function and other related singular functions is M. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions*, University Press, Cambridge, 1958. A more comprehensive account is found in A. H. Zemanian, *Distribution Theory and Transform Analysis*, McGraw-Hill, New York, 1965.

$\delta(x, x')$ and $\delta(x + a, x' + a)$ are equivalent. a is arbitrary; if we set $a = -x'$, it becomes clear that $\delta(x, x')$ depends only on $x - x'$. From now on we may write $\delta(x, x') = \delta(x - x')$ and, instead of (6.4),

$$f(x') = \int_{-\infty}^{+\infty} \delta(x - x') f(x)\, dx \tag{6.5}$$

In particular, setting $x' = 0$, we get

$$f(0) = \int_{-\infty}^{+\infty} \delta(x') f(x')\, dx' \tag{6.6}$$

From this we see that effectively $\delta(x) = 0$ except at $x = 0$.

If $f(x)$ is an odd function, $f(0) = 0$, hence $\delta(x)$ must be even:

$$\delta(-x) = \delta(x) \tag{6.7}$$

An equation like this, involving delta functions, is tacitly understood to imply that the expression on either side can be used equivalently in an integral like (6.6).

It is in this sense that we may, for example, compare Fourier's integral formula

$$f(x') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} e^{iu(x-x')} f(x)\, dx \tag{6.8}$$

with (6.5) to infer the equivalence

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{iu(x-x')}\, du \tag{6.9}$$

The integral on the right-hand side of (6.9) does not exist by any of the conventional definitions of an integral. Yet it is convenient to admit this equality as meaningful with the important proviso that the entities which are being equated must be used only in conjunction with a well-behaved function $f(x)$ under an integral sign. Physically, (6.9) may be interpreted as the superposition with equal amplitudes and phases of simple harmonic oscillations of all frequencies. The contributions to the Fourier integral completely cancel by destructive interference unless the argument vanishes, i.e., $x = x'$.

If condition (6.6) is applied to a simple function defined such that $f(x) = 1$ for $x_1 < x < x_2$, and $f(x) = 0$ outside the interval (x_1, x_2), we see that the delta function must satisfy the test

$$\int_{x_1}^{x_2} \delta(x)\, dx = \begin{cases} 0 & \text{if } x = 0 \text{ lies outside } (x_1, x_2) \\ 1 & \text{if } x_1 < 0 < x_2 \end{cases} \tag{6.10}$$

Exercise 6.1. By introducing suitable limiting processes in (6.9), show that the following expressions are all alternative representations of the delta function:

$$\delta(x) = \frac{1}{\sqrt{\pi}} \lim_{\varepsilon \to 0} \frac{1}{\sqrt{\varepsilon}} \exp\left(-\frac{x^2}{\varepsilon}\right) \tag{6.11a}$$

$$\delta(x) = \frac{1}{\pi} \lim_{\varepsilon \to 0} \frac{\varepsilon}{x^2 + \varepsilon^2} \tag{6.11b}$$

$$\delta(x) = \frac{1}{\pi} \lim_{N \to \infty} \frac{\sin Nx}{x} \tag{6.11c}$$

(Do not worry about the legitimacy of freely interchanging integrations and limiting processes. Assume[3] that $\varepsilon > 0$.)

Show that the functions (6.11) as well as the representation

$$\delta(x) = \frac{1}{2} \frac{d^2}{dx^2} |x| \tag{6.12}$$

meet the test (6.10). Invent a few other simple representations of the delta function.

Exercise 6.2. Prove that if a is a real constant, but $a \neq 0$, then

$$\delta(ax) = \frac{1}{|a|} \delta(x) \tag{6.13}$$

Also show that

$$f(x)\delta(x - a) = f(a)\delta(x - a) \tag{6.14}$$

A useful relation can be established for the delta function of a function $g(x)$. $\delta(g(x))$ vanishes except near the zeros of $g(x)$. If $g(x)$ is analytic near its zeros, x_i, the approximation $g(x) \approx g'(x_i)(x - x_i)$ may be used for $x \approx x_i$. From the definition (6.5) and from (6.13) we infer the equivalence

$$\delta(g(x)) = \sum_i \frac{1}{|g'(x_i)|} \delta(x - x_i) \tag{6.15}$$

provided that $g'(x_i) \neq 0$.

Exercise 6.3. Prove that, if $a \neq b$,

$$\delta((x - a)(x - b)) = \frac{1}{|a - b|} [\delta(x - a) + \delta(x - b)] \tag{6.16}$$

[3] Small ("infinitesimal") quantities like ε will be assumed to be *positive* everywhere in this book without special notice.

A very useful formula follows from the identity

$$\frac{1}{\omega \pm i\varepsilon} = \frac{\omega \mp i\varepsilon}{\omega^2 + \varepsilon^2} = \frac{\omega}{\omega^2 + \varepsilon^2} \mp \frac{i\varepsilon}{\omega^2 + \varepsilon^2} \tag{6.17}$$

The second term leads to a delta function [see (6.11*b*)] and the first term on the right-hand side becomes $1/\omega$ as $\varepsilon \to 0$, except if $\omega = 0$. If $f(\omega)$ is a well-behaved function, we have evidently

$$\begin{aligned}\lim_{\varepsilon\to 0} \int_{-\infty}^{+\infty} f(\omega) \frac{\omega}{\omega^2 + \varepsilon^2}\, d\omega \\ &= \lim_{\varepsilon\to 0} \int_{-\infty}^{-\varepsilon} f(\omega) \frac{d\omega}{\omega} + \lim_{\varepsilon\to 0} \int_{\varepsilon}^{+\infty} f(\omega) \frac{d\omega}{\omega} + \lim_{\varepsilon\to 0} \int_{-\varepsilon}^{\varepsilon} f(\omega) \frac{\omega\, d\omega}{\omega^2 + \varepsilon^2} \\ &= \mathsf{P}\int_{-\infty}^{+\infty} f(\omega) \frac{d\omega}{\omega} + f(0) \lim_{\varepsilon\to 0} \int_{-\varepsilon}^{\varepsilon} \frac{\omega\, d\omega}{\omega^2 + \varepsilon^2}\end{aligned}$$

where P denotes the *Cauchy principal value*.[4] The last integral vanishes because the integrand is an odd function of ω. Hence, provided that the expression is used in an integrand in conjunction with a well-behaved function of ω, we have the effective equality

$$\lim_{\varepsilon\to 0} \frac{1}{\omega \pm i\varepsilon} = \mathsf{P}\frac{1}{\omega} \mp i\pi\, \delta(\omega) \tag{6.18}$$

In addition to the delta function, it is convenient to introduce the unit *step function* $\eta(x)$ by defining

$$\eta(x) = \int_{-\infty}^{x} \delta(x')\, dx' = \begin{cases} 0 & x < 0 \\ 1 & x > 0 \end{cases} \tag{6.19}$$

Exercise 6.4. Prove that ($\varepsilon > 0$)

$$\frac{1}{i\omega + \varepsilon} = \int_{-\infty}^{+\infty} e^{-(i\omega+\varepsilon)x} \eta(x)\, dx \tag{6.20}$$

and

$$\eta(x) = \frac{1}{2} + \frac{1}{2\pi i} \mathsf{P}\int_{-\infty}^{+\infty} \frac{e^{i\omega x}}{\omega}\, d\omega \tag{6.21}$$

3. ***Normalization of Free Particle Wave Functions.*** The delta function can now be used to fix the normalization of the free particle wave functions in a simple way. Let

$$\psi_k(x) = C(k) e^{ikx} \tag{6.22}$$

where k may be positive or negative.

[4] See E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, p. 75, University Press, Cambridge, 1946.

These functions are said to be subject to *k-normalization* if

$$\int_{-\infty}^{+\infty} \psi_k^*(x)\psi_{k'}(x)\,dx = \delta(k - k') \tag{6.23}$$

Equation (6.23) gives not only the normalization; it also expresses the orthogonality of the eigenfunctions of (6.1) which belong to different values of k. Comparing (6.9) and (6.23), we find

$$|C(k)| = \frac{1}{\sqrt{2\pi}}$$

or, if the arbitrary phase of $C(k)$ is chosen to be zero,

$$C(k) = \frac{1}{\sqrt{2\pi}} \tag{6.24}$$

Similarly, we speak of *p-normalization* if

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp\left(\frac{i}{\hbar} px\right) = \frac{1}{\sqrt{h}} \exp\left(\frac{i}{\hbar} px\right) \tag{6.25}$$

so that

$$\int_{-\infty}^{+\infty} \psi_p^*(x)\psi_{p'}(x)\,dx = \delta(p - p')$$

Still other normalizations are often used. A particularly common one is the *energy normalization* of the eigenfunctions

$$A(E)e^{ikx} \qquad \text{and} \qquad B(E)e^{-ikx} \qquad (k > 0)$$

the normalization conditions being

$$\int_{-\infty}^{+\infty} A^*(E)A(E')e^{i(k'-k)x}\,dx = \delta(E - E') \tag{6.26a}$$

and

$$\int_{-\infty}^{+\infty} B^*(E)B(E')e^{-i(k'-k)x}\,dx = \delta(E - E') \tag{6.26b}$$

Let us work out (6.26*a*), remembering that

$$\hbar k = \sqrt{2\mu E}, \qquad \hbar k' = \sqrt{2\mu E'}$$

With (6.9), (6.13), and (6.14) we can write (6.26*a*) as

$$2\pi\,|A(E)|^2 \frac{\hbar}{\sqrt{2\mu}}\,\delta(\sqrt{E} - \sqrt{E'}) = \delta(E - E')$$

If $E \neq 0$, (6.15) gives

$$\delta(\sqrt{E} - \sqrt{E'}) = 2\sqrt{E}\,\delta(E - E')$$

Hence,

$$|A(E)|^2 = \sqrt{\frac{\mu}{2E}}\frac{1}{2\pi\hbar} = \frac{\mu}{hp} = \frac{1}{vh}$$

A similar calculation gives $|B(E)|^2$; hence, if the phases are chosen equal to zero, the energy normalized eigenfunctions for the free particle in one dimension are ($k > 0$)

$$\left(\frac{\mu}{8\pi^2\hbar^2 E}\right)^{1/4} e^{\pm ikx} \tag{6.27}$$

It is important to observe that any two eigenfunctions (6.27) with different signs in the exponent (representing waves propagating in opposite directions) are orthogonal, whether they belong to the same energy or not.

Again, as in the case of the harmonic oscillator, an arbitrary initial wave function can be expanded in terms of the free particle eigenfunctions. The *Fourier integral theorem* is the appropriate expansion formula, and the conditions under which it holds tell us how "arbitrary" the initial wave function can be.

Fourier analysis teaches us that there are alternative methods of constructing complete sets of free particle wave functions. They are defined by imposing certain boundary conditions on the solutions (6.2). A particularly useful set is obtained, if we require the eigenfunctions to satisfy *periodic boundary conditions* by demanding that the wave function assume the same value at any two points which are separated by a basic interval of length L. A suitable set of such eigenfunctions is again of the form (6.22), but the periodicity condition restricts the allowed values of k to a sequence of discrete numbers, expressible as

$$k = \frac{2\pi}{L}n \qquad (n = 0, \pm 1, \pm 2, \ldots) \tag{6.28}$$

Hence, if we subject the solutions of the Schrödinger equation to periodic boundary conditions, we obtain a discrete spectrum of energy eigenvalues

$$E = \frac{2\pi^2\hbar^2}{\mu L^2}n^2 \tag{6.29}$$

and each eigenvalue, except $E = 0$, is doubly degenerate. The eigenfunctions may now be normalized, and it is customary to do so by requiring that

$$\int_0^L |\psi|^2\, dx = 1$$

Hence,

$$\psi = \frac{1}{\sqrt{L}}e^{ikx} \tag{6.30}$$

According to the theorems about *Fourier series*, any function defined between $x = 0$ and $x = L$ may be expanded in terms of these functions.

From (6.29) we obtain, for $n \gg \Delta n$,

$$\Delta E = E(n + \Delta n) - E(n) = \frac{2\pi^2\hbar^2}{\mu L^2}[2n\,\Delta n + (\Delta n)^2] \sim \frac{2E}{n}\Delta n$$

We conclude that owing to the degeneracy the number of energy eigenstates per unit energy interval is approximately

$$\frac{2|\Delta n|}{\Delta E} \sim \frac{n}{E} = \sqrt{\frac{2\mu}{E}}\frac{L}{h}$$

hence, is inversely proportional to the square root of the energy. The number of states per unit momentum interval is given by

$$\frac{\Delta n}{\Delta p} = \frac{1}{\hbar}\frac{\Delta n}{\Delta k} = \frac{L}{h}$$

In statistical mechanics this last equation is somewhat loosely interpreted by saying: "The number of states per unit momentum interval and per unit length is $1/h$." Conversely, a volume h in the phase space of x and p is ascribed to each state.

4. *The Potential Step.* Next in order of increasing complexity is the potential step $V(x) = V_0\eta(x)$ as shown in Figure 6.3. There is no physically acceptable solution for $E < 0$ because of the general theorem that E can never be less than the absolute minimum of $V(x)$. Classically this is obvious. But, as the examples of the harmonic oscillator and the free particle have already shown us, it is also true in quantum mechanics despite the possibility of penetration

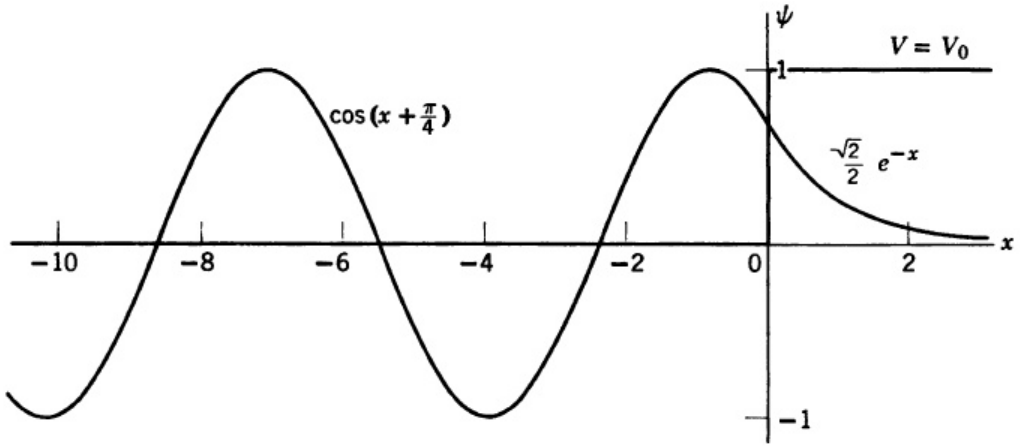


Figure 6.3. Eigenfunction for the potential step $V(x) = V_0\eta(x)$ corresponding to an energy $E = V_0/2$.

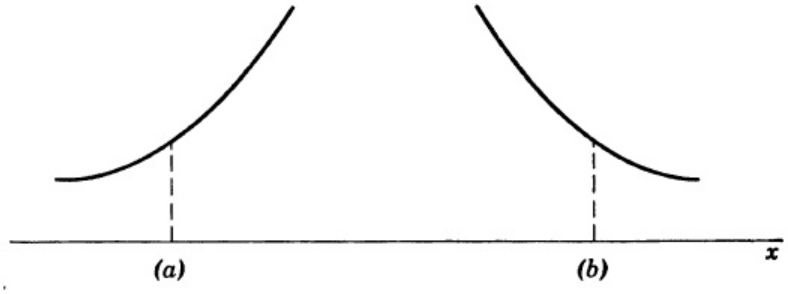


Figure 6.4. Shape of the wave function in the nonclassical region.

into classically inaccessible regions. We can prove the theorem by considering the real solutions of the Schrödinger equation (see Exercise 4.7)

$$-\frac{\hbar^2}{2\mu}\psi'' + [V(x) - E]\psi = 0$$

If $V(x) > E$ for *all* x, ψ'' has the same sign as ψ. Hence, if ψ is positive at some point x, the wave function has one of the two shapes shown in Figure 6.4, depending on whether the slope is positive or negative. In Figure 6.4*a* ψ can never bend down to be finite as $x \to \infty$. In Figure 6.4*b* ψ diverges as $x \to -\infty$. Hence, there must always be some region where $E > V(x)$ and where the particle could be found classically.

Now we consider the potential step with $0 < E < V_0$. Classically a particle of this energy, if it were incident from the left, would move freely until reflected at the potential step. Conservation of energy requires it to turn around, changing the sign of its momentum.

The Schrödinger equation has the solution

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & (x < 0) \\ Ce^{-\kappa x} & (x > 0) \end{cases} \tag{6.31}$$

Here

$$\hbar k = \sqrt{2\mu E} \qquad \hbar\kappa = \sqrt{2\mu(V_0 - E)}$$

The second linearly independent solution for $x > 0$, $e^{\kappa x}$, has been omitted because it is in conflict with the boundary condition that ψ remain finite as $x \to \infty$. Since one of the two linearly independent solutions is excluded, the stationary states for $E < V_0$ are nondegenerate.[5]

By matching the wave function and its slope at the discontinuity of the potential, $x = 0$, we have

$$A + B = C$$
$$ik(A - B) = -\kappa C$$

[5] See Chapter 5, Footnote 4.

or

$$\frac{B}{A} = \frac{ik + \kappa}{ik - \kappa} = e^{i\alpha} \qquad (\alpha\text{: real})$$
$$\frac{C}{A} = \frac{2ik}{ik - \kappa} = 1 + e^{i\alpha} \tag{6.32}$$

Substituting these values into (6.31), we obtain

$$\psi = \begin{cases} 2Ae^{i\alpha/2} \cos\left(kx - \frac{\alpha}{2}\right) & (x < 0) \\ 2Ae^{i\alpha/2} \cos\frac{\alpha}{2}\ e^{-\kappa x} & (x > 0) \end{cases} \tag{6.33}$$

in agreement with the remark made in Section 5 of Chapter 4 that the wave function in the case of no degeneracy is real except for an arbitrary constant factor. Hence, a graph may be drawn of such a wave function (Figure 6.3). The classical turning point ($x = 0$) is a point of inflection of the wave function. The oscillatory and the exponential portions can be joined smoothly at $x = 0$ for all values of E between 0 and V_0: the energy spectrum is continuous.

The solution (6.31) can be given a straightforward interpretation. It represents a plane wave incident from the left with an amplitude A and a reflected wave which propagates toward the left with an amplitude B. According to (6.32), $|A|^2 = |B|^2$; hence the reflection is *total*. Although ψ has a finite value in the region to the right of the potential step, there is no permanent penetration. A wave packet which is a superposition of eigenfunctions (6.31) could be constructed to represent a particle incident from the left. This packet would move classically, being reflected at the wall and giving again a vanishing probability of finding the particle in the region of positive x after the wave packet has receded.

These remarks can perhaps be better understood if we observe that for one-dimensional motion the conservation of probability leads to particularly transparent consequences. For a stationary state (4.2) reduces to $dj/dx = 0$. Hence, the current density

$$j = \frac{\hbar}{2\mu i}\left[\psi^* \frac{d\psi}{dx} - \frac{d\psi^*}{dx}\psi\right] \tag{6.34}$$

has the same value at all points x. j, when calculated with the wave function (6.33), is seen to vanish, as it does for any essentially real wave function. Hence, there is no net current anywhere at all. To the left of the potential step the relation $|A|^2 = |B|^2$ insures that incident and reflected probability currents cancel one another. If there is no current, there is no net momentum in the

state (6.31). In order to observe the particle in the exponential tail, it must be localized within a distance of order $\Delta x \simeq 1/\kappa$. Hence, its momentum must be uncertain by

$$\Delta p > \hbar/\Delta x \simeq \hbar\kappa = \sqrt{2\mu(V_0 - E)}$$

The particle of energy E can thus be located in the nonclassical region only if it is given an energy $V_0 - E$, sufficient to raise it into the classically allowed region.

The case of an infinitely high potential barrier ($V_0 \to \infty$ or $\kappa \to \infty$) deserves special attention. From (6.31) it follows that in this limiting case $\psi(x) \to 0$ in the region under the barrier, no matter what value the coefficient C may have. According to (6.32), the joining conditions for the wave function at $x = 0$ now reduce formally to

$$\lim_{\kappa\to\infty} \frac{B}{A} = -1, \qquad \lim_{\kappa\to\infty} \frac{C}{A} = 0$$

or $A + B = 0$ and $C = 0$ as $V_0 \to \infty$. These equations show that at a point where the potential makes an infinite jump the wave function must vanish, whereas its slope may jump discontinuously from a finite value $2ikA$ to zero.[6]

We next examine the quantum mechanics of a particle which encounters the potential step in one dimension with an energy $E > V_0$. Classically this particle passes the potential step with altered velocity but no change of direction. The particle could be incident either from the right or from the left. The solutions of the Schrödinger equation are now oscillatory in both regions; hence, to each value of the energy correspond two linearly independent, degenerate eigenfunctions. For the physical interpretation their explicit construction is best accomplished by specializing the general solution:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & (x < 0) \\ Ce^{ik_1x} + De^{-ik_1x} & (x > 0) \end{cases} \tag{6.35}$$

where $\hbar k = \sqrt{2\mu E}$ and $\hbar k_1 = \sqrt{2\mu(E - V_0)}$. Two useful particular solutions are obtained by setting $D = 0$, or $A = 0$. The first of these represents a wave incident from the left. Reflection occurs at the potential step, but there is also transmission to the right. The second particular solution represents incidence and transmission from right to left and reflection toward the right.

We consider here only the first case ($D = 0$). The remaining constants are related by the condition for smooth joining at $x = 0$,

$$A + B = C \qquad \text{and} \qquad k(A - B) = k_1C$$

[6] The discontinuity of the slope is not in conflict with the condition of smooth joining derived for *finite* jumps of the potential.

from which we solve

$$\frac{B}{A} = \frac{k - k_1}{k + k_1} \quad \text{and} \quad \frac{C}{A} = \frac{2k}{k + k_1} \tag{6.36}$$

The current density is again constant, but its value is no longer zero. Instead,

$$j = \frac{\hbar k}{\mu}(|A|^2 - |B|^2) \qquad (x < 0)$$

$$j = \frac{\hbar k_1}{\mu}|C|^2 \qquad (x > 0)$$

The equality of these values is assured by (6.36). We thus have

$$\frac{|B|^2}{|A|^2} + \frac{k_1}{k}\frac{|C|^2}{|A|^2} = 1 \tag{6.37}$$

In analogy to optics the first term in this sum is called the *reflection coefficient*, the second is the *transmission coefficient*. We have

$$R = \frac{|B|^2}{|A|^2} = \frac{(k - k_1)^2}{(k + k_1)^2} \tag{6.38}$$

$$T = \frac{k_1}{k}\frac{|C|^2}{|A|^2} = \frac{4kk_1}{(k + k_1)^2} \tag{6.39}$$

Equation (6.37) assures us that $R + T = 1$. R and T depend only on the ratio E/V_0.

For a wave packet incident from the left the presence of reflection means that the wave packet may, when it arrives at the potential step, split into two parts, provided that its average energy is close to V_0. This splitting up of the wave packet is a distinctly nonclassical effect which affords an argument against the early attempts to interpret the wave function as measuring the matter (or charge) density of the particle which it accompanies. For the splitting up of the wave packet would then imply a physical breakup of the particle, and this would be very difficult to reconcile with the facts of observation. After all, electrons and other particles are always found as complete entities with the same distinct properties. On the other hand, there is no contradiction between the splitting up of a wave packet and the probability interpretation of the wave function.

Exercise 6.4. Show that the coefficients for reflection and transmission at a potential step are the same for a wave incident from the right as for a wave incident from the left.

5. *The Rectangular Potential Barrier.* In our study of more and more complicated potential forms, we now reach a very important case, the rectangular *potential barrier* (Figure 6.5). There is a slight advantage in placing the coordinate origin at the center of the barrier so that $V(x)$ is an *even* function of x. Owing to the quantum mechanical penetration of a barrier, a case of great interest is that of $E < V_0$. The particle is free for $x < -a$ and $x > a$. For this reason the rectangular potential barrier simulates, albeit schematically, the scattering of a free particle from any potential.

We can immediately write down the general solution of the Schrödinger equation for $E < V_0$:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & (x < -a) \\ Ce^{-\kappa x} + De^{\kappa x} & (-a < x < a) \\ Fe^{ikx} + Ge^{-ikx} & (a < x) \end{cases} \tag{6.40}$$

where again $\hbar k = \sqrt{2\mu E}$, $\hbar\kappa = \sqrt{2\mu(V_0 - E)}$. The boundary conditions at $x = -a$ require

$$\begin{aligned} Ae^{-ika} + Be^{ika} &= Ce^{\kappa a} + De^{-\kappa a} \\ Ae^{-ika} - Be^{ika} &= \frac{i\kappa}{k}(Ce^{\kappa a} - De^{-\kappa a}) \end{aligned} \tag{6.41}$$

These linear homogeneous relations between the coefficients A, B, C, D are conveniently expressed in terms of matrices:

$$\begin{pmatrix} A \\ B \end{pmatrix} = \frac{1}{2}\begin{pmatrix} \left(1 + \frac{i\kappa}{k}\right)e^{\kappa a + ika} & \left(1 - \frac{i\kappa}{k}\right)e^{-\kappa a + ika} \\ \left(1 - \frac{i\kappa}{k}\right)e^{\kappa a - ika} & \left(1 + \frac{i\kappa}{k}\right)e^{-\kappa a - ika} \end{pmatrix}\begin{pmatrix} C \\ D \end{pmatrix}$$

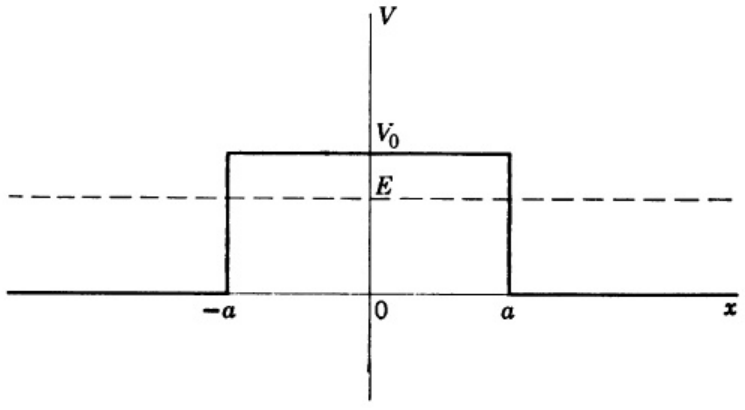


Figure 6.5. Rectangular potential barrier, height V_0, width $2a$.

The joining conditions at $x = a$ are similar. They yield

$$\begin{pmatrix} C \\ D \end{pmatrix} = \frac{1}{2}\begin{pmatrix} \left(1 - \frac{ik}{\kappa}\right)e^{\kappa a + ika} & \left(1 + \frac{ik}{\kappa}\right)e^{\kappa a - ika} \\ \left(1 + \frac{ik}{\kappa}\right)e^{-\kappa a + ika} & \left(1 - \frac{ik}{\kappa}\right)e^{-\kappa a - ika} \end{pmatrix}\begin{pmatrix} F \\ G \end{pmatrix}$$

Combining the last two equations, we obtain the relation between the wave function on both sides of the barrier:

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \left(\cosh 2\kappa a + \frac{i\varepsilon}{2}\sinh 2\kappa a\right)e^{2ika} & \frac{i\eta}{2}\sinh 2\kappa a \\ -\frac{i\eta}{2}\sinh 2\kappa a & \left(\cosh 2\kappa a - \frac{i\varepsilon}{2}\sinh 2\kappa a\right)e^{-2ika} \end{pmatrix}\begin{pmatrix} F \\ G \end{pmatrix} \tag{6.42}$$

where the abbreviated notation

$$\varepsilon = \frac{\kappa}{k} - \frac{k}{\kappa}, \qquad \eta = \frac{\kappa}{k} + \frac{k}{\kappa} \tag{6.43}$$

has been used.

Exercise 6.5. Calculate the determinant of the 2×2 matrix in (6.42).

A particular solution of interest is obtained from (6.42) by letting $G = 0$. This represents a wave incident from the left, and transmitted through the barrier to the right. A reflected wave whose amplitude is B is also present. We calculate easily:

$$\frac{F}{A} = \frac{e^{-2ika}}{\cosh 2\kappa a + i(\varepsilon/2)\sinh 2\kappa a} \tag{6.44}$$

The square of the absolute value of this quantity is the transmission coefficient for the barrier. It assumes an especially simple form for a high and wide barrier which transmits poorly ($\kappa a \gg 1$). In first approximation,

$$\cosh 2\kappa a \approx \sinh 2\kappa a \approx \tfrac{1}{2}e^{2\kappa a}$$

hence,

$$T = \left|\frac{F}{A}\right|^2 \approx 16e^{-4\kappa a}\left(\frac{k\kappa}{k^2 + \kappa^2}\right)^2 \tag{6.45}$$

The matrix which connects A and B with F and G in (6.42) has very simple properties. If we write the linear relations as

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \alpha_1 + i\beta_1 & \alpha_2 + i\beta_2 \\ \alpha_3 + i\beta_3 & \alpha_4 + i\beta_4 \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} \tag{6.46}$$

and compare this with (6.42), we observe that the eight real numbers α and β in the matrix satisfy the conditions

$$\alpha_1 = \alpha_4, \qquad \beta_1 = -\beta_4, \qquad \alpha_2 = \alpha_3 = 0, \qquad \beta_2 = -\beta_3 \tag{6.47}$$

These five equations reduce the number of independent variables on which the matrix depends from eight to three. As can be seen from (6.42) and Exercise 6.5, we must add to this an equation expressing the fact that the determinant of the matrix is equal to unity. Using (6.47), this condition reduces to

$$\alpha_1^2 + \beta_1^2 - \beta_2^2 = 1 \tag{6.48}$$

Hence, we are left with two parameters, as we must be, since the matrix depends explicitly only on the independent variables ka and κa.

Exercise 6.6. Show that (6.46) can be written as

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} e^{i\mu} \cosh \lambda & i \sinh \lambda \\ -i \sinh \lambda & e^{-i\mu} \cosh \lambda \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} \tag{6.49}$$

where λ and μ are two real parameters.

In the next section it will be shown that the conditions (6.47) and (6.48) imposed on (6.46), rather than pertaining specifically to the rectangular-shaped potential, are consequences of very general symmetry properties of the physical system at hand.

6. ***Symmetries and Invariance Properties.*** Since the rectangular barrier of Figure 6.5 is a real potential and symmetric about the origin, the Schrödinger equation is invariant under time reversal and space reflection. We can exploit these properties to derive the general form of the matrix linking the incident with the transmitted wave.

We recapitulate the form of the general solution of the Schrödinger equation:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & (x < -a) \\ Ce^{-\kappa x} + De^{\kappa x} & (-a < x < a) \\ Fe^{ikx} + Ge^{-ikx} & (a < x) \end{cases} \tag{6.40}$$

We need not reproduce here the joining conditions at $x = -a$ and $x = a$, because we want to see how far we can proceed without these conditions. Nevertheless, it is clear that the joining conditions lead to two linear homogeneous relations between the coefficients A, B, F, and G. If we regard the wave function on one side of the barrier, say for $x > a$, as given, then these relations are linear equations expressing the coefficients A and B in terms of F and G. Hence a matrix M exists such that

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} \tag{6.50}$$

An equivalent representation expresses the coefficients B and F of the *outgoing* waves in terms of the coefficients A and G of the *incoming* waves by the matrix relation

$$\begin{pmatrix} B \\ F \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix} \tag{6.51}$$

Whereas the representation in terms of the S matrix is more readily generalized to three-dimensional situations, the M matrix is more appropriate in one-dimensional problems and is therefore used in Sections 5, 7, and 8 of this chapter. On the other hand, the symmetry properties are best formulated in terms of the S matrix.

The S and M matrices can be simply related if conservation of probability is invoked. As was shown in Section 6.4, in a one-dimensional stationary state the probability current density j must be independent of x. Applying expression (6.34) to the wave function (6.40), we obtain the condition

$$|A|^2 - |B|^2 = |F|^2 - |G|^2 \qquad \text{or} \qquad |B|^2 + |F|^2 = |A|^2 + |G|^2$$

as expected, since $|A|^2$ and $|F|^2$ measure the probability flow to the right, while $|B|^2$ and $|G|^2$ measure the flow in the opposite direction. Using matrix notation, we can write this as

$$(B^* \; F^*) \begin{pmatrix} B \\ F \end{pmatrix} = (A^* \; G^*) S^* S \begin{pmatrix} A \\ G \end{pmatrix} = (A^* \; G^*) \begin{pmatrix} A \\ G \end{pmatrix}$$

where $\tilde{S}$ denotes the transpose matrix of S, and S^* the complex conjugate. It follows that S must obey the condition

$$\tilde{S}^* S = 1 \tag{6.52}$$

with I denoting the unit matrix in two dimensions. If the *Hermitian conjugate* $S^\dagger$ of a matrix S is defined by

$$S^\dagger = \tilde{S}^* = \begin{pmatrix} S_{11}^* & S_{21}^* \\ S_{12}^* & S_{22}^* \end{pmatrix} \tag{6.53}$$

equation (6.52) implies the statement that the inverse of S must be the same as its Hermitian conjugate. Such a matrix is said to be *unitary*.

The elements of the matrix S are therefore subject to the following constraints:

$$|S_{11}| = |S_{22}| \quad \text{and} \quad |S_{12}| = |S_{21}| \tag{6.54}$$

$$|S_{11}|^2 + |S_{12}|^2 = 1 \tag{6.55}$$

and

$$S_{11}S_{12}^* + S_{21}S_{22}^* = 0 \tag{6.56}$$

Since the potential is real, the Schrödinger equation has, according to Section 4.5, in addition to (6.40) the time-reversed solution

$$\psi_1(x) = \begin{cases} A^* e^{-ikx} + B^* e^{ikx} & (x < -a) \\ C^* e^{-\kappa x} + D^* e^{\kappa x} & (-a < x < a) \\ F^* e^{-ikx} + G^* e^{ikx} & (a < x) \end{cases} \tag{6.57}$$

Comparison of this solution with (6.40) shows that effectively the directions of motion have been reversed and the coefficient A has been interchanged with B^*, and F with G^*. Hence, in (6.51) we may make the replacements $A \leftrightarrow B^*$ and $F \leftrightarrow G^*$, and obtain an equally valid equation

$$\begin{pmatrix} A^* \\ G^* \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} B^* \\ F^* \end{pmatrix} \tag{6.58}$$

Equations (6.58) and (6.51) can be combined to yield the condition

$$S^*S = I \tag{6.59}$$

This condition in conjunction with the unitarity relation (6.52) implies that the S matrix must be *symmetric* as a consequence of time reversal symmetry. If S is unitary and symmetric, it is easy to verify by comparing equations (6.50) and (6.51) that the M matrix assumes the form:

$$M = \begin{pmatrix} \dfrac{1}{S_{12}} & \dfrac{S_{11}^*}{S_{12}^*} \\ \dfrac{S_{11}}{S_{12}} & \dfrac{1}{S_{12}^*} \end{pmatrix} \tag{6.60}$$

with

$$\det M = (1 - |S_{11}|^2)/|S_{12}|^2 = 1$$

Since the potential is an even function of x, another solution is obtained by replacing x in (6.40) by $-x$. The substitution gives

$$\psi_2(x) = \begin{cases} Ae^{-ikx} + Be^{ikx} & (x > a) \\ Ce^{\kappa x} + De^{-\kappa x} & (a > x > -a) \\ Fe^{-ikx} + Ge^{ikx} & (-a > x) \end{cases} \tag{6.61}$$

If Ge^{ikx} is the wave incident on the barrier from the left, Be^{ikx} is the transmitted and Fe^{-ikx} the reflected wave in (6.61). Ae^{-ikx} is incident from the right. Hence, in (6.51) we may make the replacements $A \leftrightarrow G$ and $B \leftrightarrow F$, and obtain

$$\begin{pmatrix} F \\ B \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} G \\ A \end{pmatrix}$$

This relation can also be written as

$$\begin{pmatrix} B \\ F \end{pmatrix} = \begin{pmatrix} S_{22} & S_{21} \\ S_{12} & S_{11} \end{pmatrix} \begin{pmatrix} A \\ G \end{pmatrix}$$

Hence, invariance under reflection implies the symmetry relations

$$S_{11} = S_{22} \qquad \text{and} \qquad S_{12} = S_{21} \tag{6.62}$$

If conservation of probability, time reversal invariance, and invariance under space reflection are simultaneously demanded, the matrix M has the structure

$$M_{11} = M_{22}^*, \qquad M_{12} = -M_{12}^* = -M_{21} = M_{21}^*, \qquad \det M = 1$$

The matrix in (6.42) and (6.49) satisfies precisely these conditions. We thus see that the conditions (6.47) and (6.48) are the result of very general properties, shared by all potentials that are symmetric with respect to the origin and vanish for large values of $|x|$. For all such potentials the solution of the Schrödinger equation must be asymptotically of the form

$$\psi(x) \sim Ae^{ikx} + Be^{-ikx} \quad \text{as } x \to -\infty$$

and

$$\psi(x) \sim Fe^{ikx} + Ge^{-ikx} \quad \text{as } x \to +\infty$$

By virtue of the general arguments just advanced, these two portions of the eigenfunction are related by the equation[7]

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \alpha_1 + i\beta_1 & i\beta_2 \\ -i\beta_2 & \alpha_1 - i\beta_1 \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix}$$

with the real parameters α_1, β_1, and β_2 subject to the additional constraint

$$\alpha_1^2 + \beta_1^2 - \beta_2^2 = 1$$

Although the restrictions that various symmetries impose on the S or M matrix usually complement each other, they are occasionally redundant. For instance, in the simple one-dimensional problem treated in this section, invariance under reflection, if applicable, guarantees that the S matrix is symmetric [Equation (6.62)], thus yielding a condition that is equally prescribed by invariance under time reversal together with probability conservation.

A significant aspect of the matrix method of this section is that it allows a neat separation between the initial conditions, which can be adapted to the requirements of any particular problem, and the matrices M and S, which do not depend on the particular structure of the wave packet used. S and M depend only on the nature of the dynamical system, the forces, and the energy. Once either one of these matrices has been worked out as a function of energy, all problems relating to the potential barrier have essentially been solved. For example, the transmission coefficient T is given by $|F|^2/|A|^2$ if $G = 0$, and therefore

$$T = \frac{1}{|M_{11}|^2} = |S_{21}|^2 \tag{6.63}$$

We shall encounter other uses of the M and S matrices in subsequent sections. Eventually, in Chapter 19, we shall see that similar methods are pertinent in the general theory of collisions, where the S or *scattering matrix* plays a central role. The work of this section is S-matrix theory in its most elementary form.

[7] The same concepts can be generalized to include long-range forces. All that is needed to define a matrix M with the properties (6.47) and (6.48) is that the two linearly independent fundamental solutions of the Schrödinger equation have the asymptotic property

$$\psi_1(-x) = \psi_2(x) = \psi_1^*(x)$$

For a real even potential function $V(x)$ this can always be accomplished by choosing

$$\psi_{1,2}(x) = \psi_{\text{even}}(x) \pm i\psi_{\text{odd}}(x)$$

where ψ_{even} and ψ_{odd} are the real even and odd solutions.

Exercise 6.7. Noting that k appears in the Schrödinger equation only quadratically, prove that, as a function of k, the S matrix has the property

$$S(k)S(-k) = I \tag{6.64}$$

Derive the corresponding properties of the matrix M, and verify them in the example of Section 6.5.

Exercise 6.8. Using invariance under time reversal only, prove that at a fixed energy the value of the transmission coefficient is independent of the direction of incidence.

7. *The Periodic Potential.* With a little extra effort we can now proceed to solve the more complicated problem of a particle in the presence of a periodic potential composed of a succession of potential barriers.[8] Figure 6.2 shows a cut from this battlement-shaped potential which serves as a model of the potential to which an electron in a crystal lattice is exposed. The oversimplified shape treated here already exhibits the essential features of all such periodic potentials. As a useful idealization we assume that potential hills and valleys follow each other in periodic succession indefinitely in both directions, although in reality the number of atoms in a crystal is, of course, finite, if large. $l = 2a + 2b$ is the *period* of this potential.

The matrix method is especially well suited for treating this problem. The solution of the Schrödinger equation in the valleys, where $V = 0$ and $\hbar k = \sqrt{2\mu E}$, may be written in the form

$$\psi(x) = A_n e^{ik(x-nl)} + B_n e^{-ik(x-nl)} \tag{6.65}$$

for $a - l < x - nl < -a$. The coefficients belonging to successive values of n can be related by a matrix using the procedure and notation of the last section. Noting that the centers of the peaks have the coordinates $x = nl$, we obtain

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} \alpha_1 + i\beta_1 & i\beta_2 \\ -i\beta_2 & \alpha_1 - i\beta_1 \end{pmatrix} \begin{pmatrix} A_{n+1}e^{-ikl} \\ B_{n+1}e^{ikl} \end{pmatrix}$$

This may also be written as

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = P \begin{pmatrix} A_n \\ B_n \end{pmatrix} \tag{6.66}$$

[8] The periodic potential of Figure 6.2 is known as the *Kronig-Penney potential*. For a comprehensive treatment in the framework of solid state physics see C. Kittel, *Introduction to Solid State Physics*, third edition, John Wiley & Sons, New York, 1966.

where the matrix P is defined by

$$P = \begin{pmatrix} (\alpha_1 - i\beta_1)e^{ikl} & -i\beta_2 e^{ikl} \\ i\beta_2 e^{-ikl} & (\alpha_1 + i\beta_1)e^{-ikl} \end{pmatrix} \tag{6.67}$$

subject to the condition

$$\alpha_1^2 + \beta_1^2 - \beta_2^2 = 1 \tag{6.48}$$

By iteration we have

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = P^n \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \tag{6.68}$$

Applying these considerations to an infinite periodic lattice, we must clearly demand that as $n \to \pm\infty$ the limit of P^n should exist. This is most conveniently discussed in terms of the eigenvalue problem of the matrix P.

The eigenvalues of P are roots of the characteristic equation

$$p^2 - p \operatorname{trace} P + \det P = 0$$

or

$$p^2 - 2(\alpha_1 \cos kl + \beta_1 \sin kl)\, p + 1 = 0$$

The roots are

$$p_\pm = \tfrac{1}{2}[\operatorname{trace} P \pm \sqrt{(\operatorname{trace} P)^2 - 4}]$$

If the roots are different, the two eigenvectors are linearly independent, and two linearly independent solutions of the Schrödinger equation are obtained by identifying the initial values $\begin{pmatrix} A_0 \\ B_0 \end{pmatrix}$ with these eigenvectors:

$$P \begin{pmatrix} A_0^{(\pm)} \\ B_0^{(\pm)} \end{pmatrix} = p_\pm \begin{pmatrix} A_0^{(\pm)} \\ B_0^{(\pm)} \end{pmatrix}$$

For these particular solutions (6.68) becomes

$$\begin{pmatrix} A_n^{(\pm)} \\ B_n^{(\pm)} \end{pmatrix} = p_\pm{}^n \begin{pmatrix} A_0^{(\pm)} \\ B_0^{(\pm)} \end{pmatrix} \tag{6.69}$$

If $|\operatorname{trace} P| > 2$, p_+ and p_- are real and either $\lim_{n\to\infty} |p_\pm{}^n| \to \infty$ or $\lim_{n\to-\infty} |p_\pm{}^n| \to \infty$. Such solutions (6.69) are in conflict with the requirement that the wave function must remain finite. Hence, an acceptable solution is obtained and a particular energy value allowed only if

$$\tfrac{1}{2}\,|\operatorname{trace} P| = |\alpha_1 \cos kl + \beta_1 \sin kl| \leqslant 1$$

If this condition holds, we may write

$$p_+ = e^{ikl}, \qquad p_- = e^{-ikl} \tag{6.70}$$

thus defining a real parameter k which is related to the energy by the condition

$$\cos \mathrm{k}l = \alpha_1 \cos kl + \beta_1 \sin kl \tag{6.71}$$

For the potential shape of Figure 6.2 this can, according to (6.42), be written as

$$\cos \mathrm{k}l = \cosh 2\kappa a \cos 2kb + (\varepsilon/2) \sinh 2\kappa a \sin 2kb \tag{6.72}$$

where $\hbar\kappa = \sqrt{2\mu(V_0 - E)}$ and $E < V_0$.

Since $|\cosh 2\kappa a| \geqslant 1$, it is readily seen that all energy values for which

$$2kb = N\pi \qquad (N = \text{integer}) \tag{6.73}$$

are forbidden or are at edges of allowed bands. From the continuity of all the functions involved it follows that there must generally be forbidden ranges of energy values in the neighborhood of the discrete values determined by (6.73).

Exercise 6.9. Show that, if $E > V_0$, the eigenvalue condition for the periodic potential of Figure 6.2 becomes

$$\cos \mathrm{k}l = \cos 2k'a \cos 2kb - \frac{k'^2 + k^2}{2kk'} \sin 2k'a \sin 2kb \tag{6.74}$$

where $\hbar k' = \sqrt{2\mu(E - V_0)}$. Verify that the energies determined by the condition $(2k'a + 2kb) = N\pi$ are forbidden, and prove that $\mathrm{k} \to k$ as $E \to \infty$.

From (6.72) and (6.74) the allowed values of the energy can be calculated in terms of the constants of the potential and the parameter k. Figure 6.6 is a plot of $k^2 \propto E$ versus k for a particular choice of constants, showing that the energy spectrum consists of continuous *bands* separated by forbidden gaps. The band structure of the energy levels of electrons in a periodic lattice is a direct consequence of the wave nature of matter. It is essential to an understanding of many basic properties of the solid state of matter and indispensable in the quantum theory of electric conduction in metals. Even in its crudest and most schematic form it accounts qualitatively for the distinction between conductors and insulators. In its refined form the band theory is able to correlate a large amount of experimental data quantitatively.[9] In applications to the solid state, quantum mechanics has scored some of its greatest triumphs.

We must now look briefly at the eigenfunctions of the Schrödinger equation. In the valleys they are of the form (6.65). The coefficients of the

[9] See reference in footnote 8.

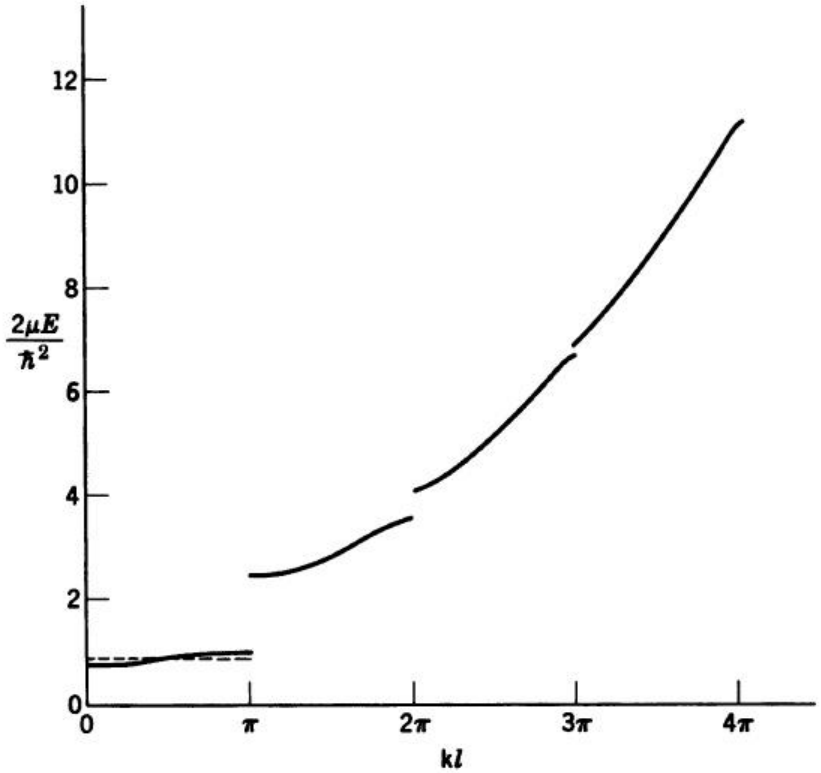


Figure 6.6. $k^2 = 2\mu E/\hbar^2$ versus k for the periodic potential of Figure 6.2 with $a = b = 1$ and $2\mu V_0/\hbar^2 = \pi^2/4$. The dashed line indicates the position of the bound energy level in a rectangular well of depth V_0 and width $2b$. The presence of infinitely many such wells in a periodic lattice produces a continuous narrow band of allowed energy levels.

plane waves for two fundamental solutions corresponding to the same energy are given by

$$\begin{pmatrix} A_n^{(+)} \\ B_n^{(+)} \end{pmatrix} = e^{ink l} \begin{pmatrix} A_0^{(+)} \\ B_0^{(+)} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} A_n^{(-)} \\ B_n^{(-)} \end{pmatrix} = e^{-ink l} \begin{pmatrix} A_0^{(-)} \\ B_0^{(-)} \end{pmatrix} \tag{6.75}$$

Because of invariance under time reversal, we may assume the relation

$$\frac{A_0^{(-)}}{B_0^{(-)}} = \left(\frac{B_0^{(+)}}{A_0^{(+)}}\right)^*$$

between the two solutions. From the eigenvalue equation for the matrix P, we obtain the ratio

$$\frac{A_0^{(+)}}{B_0^{(+)}} = \frac{\beta_2 e^{ikl}}{\alpha_1 \sin kl - \beta_1 \cos kl - \sin kl} \tag{6.76}$$

which can be used to construct the eigenfunctions:

$$\begin{aligned}\psi^{(+)} &= [\psi^{(-)}]^* \\ &= e^{ink l}\{\beta_2 e^{ik[x-(n-1/2)l]} + (\alpha_1 \sin kl - \beta_1 \cos kl - \sin \mathsf{k}l)e^{-ik[x-(n-1/2)l]}\} \\ &= e^{ikx}e^{-ik(x-nl)}\{\cdots\} = e^{ikx}u_{\mathsf{k}}(x) \qquad (6.77)\end{aligned}$$

for $a - l < x - nl < -a$. Equation (6.77) gives the eigenfunctions in the valley portions of the potential in Figure 6.2. In the hill portions the harmonic waves are replaced by increasing and decreasing exponentials, the coefficients being determined by matching the eigenfunction at hill-valley boundaries. Since the function $u_{\mathsf{k}}(x)$ defined by equation (6.77) has the periodicity property

$$u_{\mathsf{k}}(x + l) = u_{\mathsf{k}}(x)$$

the eigenfunctions (6.77) are products of harmonic plane waves with wave number k and functions $u_{\mathsf{k}}(x)$ which have the same period as the potential (Figure 6.7).

The two solutions $\psi^{(+)}$ and $\psi^{(-)}$ are linearly independent unless $\mathsf{k}l = N\pi$, N integer. In this important special case the two solutions become identical. Furthermore, since it can be shown that for these values of k

$$\alpha_1 \sin kl - \beta_1 \cos kl = \pm\beta_2 \qquad (6.78)$$

the eigenfunctions (6.77) represent standing waves. These solutions correspond to the band edges.

Exercise 6.10. Verify (6.78) for $\mathsf{k}l = N\pi$.

Although the results of this section were derived for a rectangular-shaped potential, any periodic potential yields eigenfunctions of the general form (6.77). This property is known as *Floquet's theorem* and functions of this

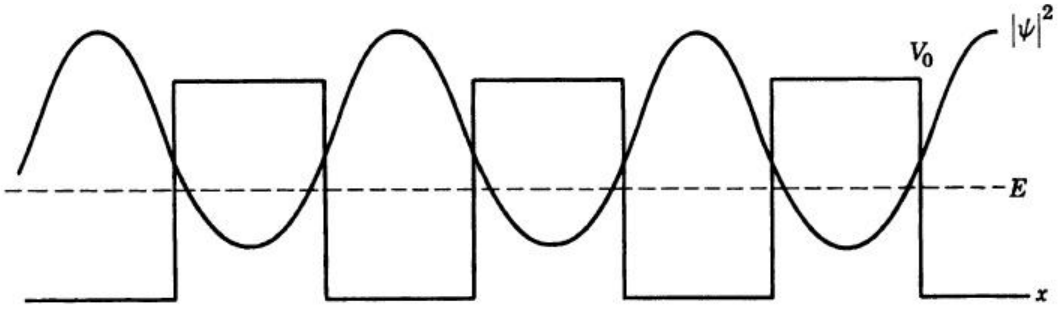


Figure 6.7. Sketch of $|\psi|^2$ for a periodic potential. $E = V_0/2$ was assumed. The curve consists of alternating sections of trigonometric and hyperbolic sine functions, joined smoothly at the discontinuities of V.

form, which play an important role in the electron theory of metals, are called *Bloch wave functions* (see Exercise 14.19).

Exercise 6.11. Prove that the periodic function $u_k(x)$ satisfies the equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2u_k}{dx^2} - \frac{i\hbar^2 k}{\mu}\frac{du_k}{dx} + \frac{\hbar^2 k^2}{2\mu}u_k + Vu_k = Eu_k \tag{6.79}$$

8. *The Square Well.* Finally, we must discuss the so-called *square* (or rectangular) *well*. It is convenient to place the origin of the x-axis in the center of the potential well, so that $V(x)$ is again an even function of x: $V = -V_0$ for $-a < x < a$, and $V = 0$ for all other values of x, or

$$V(x) = V_0[\eta(x-a) - \eta(x+a)]$$

with $V_0 > 0$.

Depending on whether the energy is positive or negative, we distinguish two separate cases. If $E > 0$, the particle is unconfined and is *scattered* by the potential; if $E < 0$, it is confined and in a *bound* state. We treat this last case first.

$-V_0 \leqslant E < 0$. Reversing our earlier notation, we now set

$$\hbar k' = \sqrt{2\mu(E+V_0)}, \qquad \hbar\kappa = \sqrt{-2\mu E} \tag{6.80}$$

The Schrödinger equation can be written as

$$\frac{d^2\psi}{dx^2} + k'^2\psi = 0 \qquad \text{inside the well} \tag{6.81a}$$

and

$$\frac{d^2\psi}{dx^2} - \kappa^2\psi = 0 \qquad \text{outside the well} \tag{6.81b}$$

As for any even potential, we may restrict the search for eigenfunctions to those of definite parity.

Inside the well we have

$$\begin{aligned} \psi &= A'\cos k'x \qquad \text{for even parity} \\ \psi &= B'\sin k'x \qquad \text{for odd parity} \end{aligned} \tag{6.82}$$

Outside we have in either case only the decreasing exponential

$$\psi = C'e^{-\kappa|x|} \tag{6.83}$$

since the wave function must not become infinite at large distances.

It is necessary to match the wave function and its first derivative at $x = a$, i.e., to require that as $\varepsilon \to 0$

$$\psi(a - \varepsilon) = \psi(a + \varepsilon) \tag{6.84}$$

and

$$[\psi'(x)]_{a-\varepsilon} = [\psi'(x)]_{a+\varepsilon} \tag{6.85}$$

Since an overall constant factor remains arbitrary until determined by normalization, these two conditions are equivalent to demanding that the *logarithmic derivative* of ψ,

$$\frac{1}{\psi}\frac{d\psi}{dx} \tag{6.86}$$

shall be continuous at $x = a$. This is a very common way of phrasing the joining conditions.

The logarithmic derivative of the outside wave function, evaluated at $x = a$, is $-\kappa$; that of the inside wave function is $-k' \tan k'a$ for the even case, and k' cotan $k'a$ for the odd case.

The transcendental equations

$$\begin{aligned} k' \tan k'a &= \kappa \qquad \text{(even)} \\ k' \operatorname{cotan} k'a &= -\kappa \qquad \text{(odd)} \end{aligned} \tag{6.87}$$

permit us to determine the allowed eigenvalues of the energy E.

The general symmetry considerations of Section 6.6 can also be extended to solutions of the Schrödinger equation with negative values of k^2 and the energy. In (6.40) we need only replace k by $i\kappa$ and κ by ik' in the regions $|x| > a$. The solution then takes the form

$$\psi(x) = \begin{cases} Ae^{-\kappa x} + Be^{\kappa x} & (x < -a) \\ Ce^{-ik'x} + De^{ik'x} & (-a < x < a) \\ Fe^{-\kappa x} + Ge^{\kappa x} & (a < x) \end{cases}$$

By applying invariance under time reversal and the principle of conservation of probability, we see that M must now be a real matrix with $\det M = 1$. The boundary conditions at large distances require that $A = G = 0$. In terms of the matrix M, we must thus demand that

$$M_{11} = 0 \tag{6.88}$$

and this equation yields the energy eigenvalues. Reflection symmetry implies that $M_{12} = \pm 1$, giving us the even and odd solutions.

Exercise 6.12. Verify the statements in the last paragraph, and also show that the S matrix as a function of energy is singular at the bound states.

Exercise 6.13. By changing V_0 into $-V_0$ in (6.42), show that, for a square well, (6.88) is equivalent to the eigenvalue conditions (6.87).

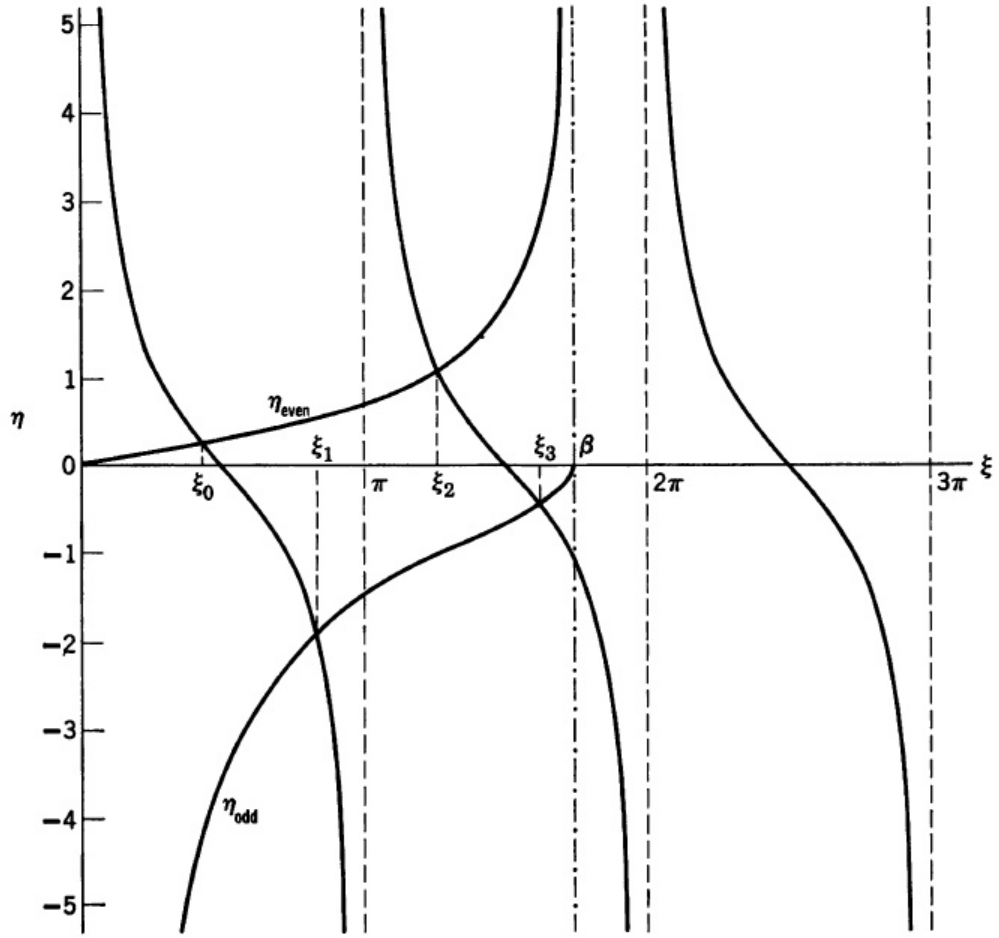


Figure 6.8. Graphical determination of the energy levels in a square well with $\beta = \sqrt{30}$.

A simple graphical method aids in visualizing the roots of (6.87). We set

$$\xi = k'a; \qquad \beta = \frac{\sqrt{2\mu V_0}}{\hbar} a; \qquad \sqrt{\beta^2 - \xi^2} = \kappa a$$

and

$$\eta = \operatorname{cotan} \xi$$

In Figure 6.8 η is plotted as a function of ξ. The required roots are found by determining the points of intersection of this curve with the curves

$$\eta_{\text{even}} = \xi(\beta^2 - \xi^2)^{-1/2} \qquad \text{(even)}$$

and

$$\eta_{\text{odd}} = \frac{-(\beta^2 - \xi^2)^{1/2}}{\xi} \equiv -\frac{1}{\eta_{\text{even}}} \qquad \text{(odd)} \tag{6.89}$$

We see that the only pertinent parameter is the value of β. By inspection of Figure 6.8 we can immediately draw several conclusions: All bound states of

the well are nondegenerate; even and odd solutions alternate as the energy increases; the number of bound states is finite and equal to $N+1$, if $N\pi/2 < \beta \leqslant (N+1)\pi/2$; if the bound states are labeled in order of increasing energy by a quantum number $n = 0, 1, \ldots, N$, even values of n correspond to even parity, odd values of n correspond to odd parity, and n denotes the number of nodes; for any square well there is always at least one even state, but there can be no odd state unless $\beta > \pi/2$.

A case of special interest is the infinitely deep well, $V_0 \to \infty$, or $\beta \to \infty$. It is apparent that the roots of the equations expressing the boundary conditions are now

$$\xi = (n+1)\frac{\pi}{2} \qquad (n = 0, 1, 2, \ldots)$$

or

$$E + V_0 = (n+1)^2 \frac{\pi^2\hbar^2}{8\mu a^2} \tag{6.90}$$

$E + V_0$, the distance in energy from the bottom of the well, is simply the kinetic energy of the particle in the well. Since $\kappa \to \infty$ as $V_0 \to \infty$ and $E \to -\infty$, the wave function itself must vanish at $x = \pm a$. There is in this limit no condition on the slope.[6] Taking into account a shift V_0 of the zero of energy and making the identification $2a = L$, the energy levels (6.90) for odd values of n coincide with the spectrum (6.29). Note that the number of states is essentially the same in either case, since there is double degeneracy in (6.29) for all but the lowest level, whereas (6.90) has no degeneracy, but between any two levels (6.29) there lies one given by (6.90) corresponding to even values of n. There is, however, no eigenstate of the infinitely deep well at $E + V_0 = 0[n = 0$ in (6.29)], because the corresponding eigenfunction vanishes.

To conclude this chapter we discuss briefly what happens to a particle incident from a great distance when it is scattered by a square well. Here $E > 0$. Actually this problem has already been solved. We may carry over the results for the potential barrier, replacing V_0 by $-V_0$ and κ by ik', where $\hbar k' = \sqrt{2\mu(E + V_0)}$. Equation (6.42) becomes

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \left(\cos 2k'a - \frac{i\varepsilon'}{2}\sin 2k'a\right)e^{2ika} & \frac{i\eta'}{2}\sin 2k'a \\ -\frac{i\eta'}{2}\sin 2k'a & \left(\cos 2k'a + \frac{i\varepsilon'}{2}\sin 2k'a\right)e^{-2ika} \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} \tag{6.91}$$

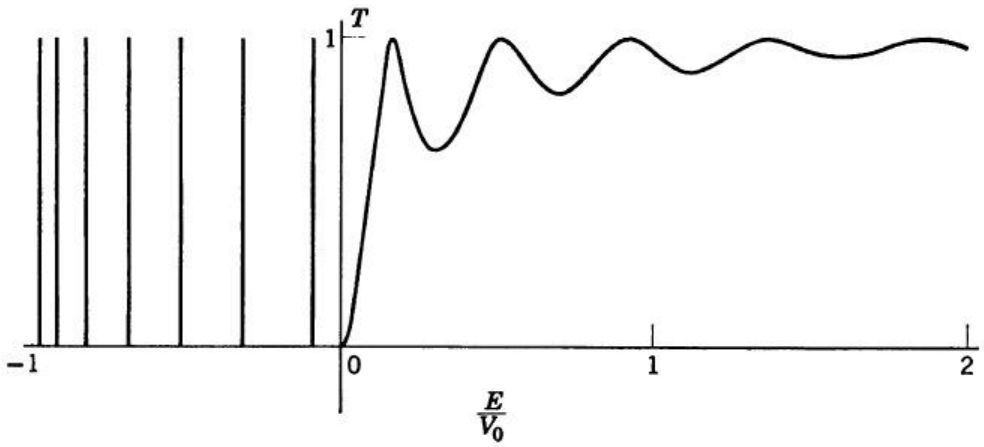


Figure 6.9. Transmission coefficient T versus E/V_0 for a square well with $\beta = 13\pi/4$. The spikes on the left are at the positions of the discrete energy levels.

where

$$\varepsilon' = \frac{k'}{k} + \frac{k}{k'}, \qquad \eta' = \frac{k}{k'} - \frac{k'}{k} \tag{6.92}$$

Equation (6.91) defines the matrix M for the square well.

According to (6.63), the transmission coefficient T is

$$T = \frac{1}{|M_{11}|^2} = \frac{1}{\cos^2 2k'a + \dfrac{\varepsilon'^2}{4}\sin^2 2k'a} \tag{6.93}$$

As $E \to \infty$, $\varepsilon' \to 2$, and $T \to 1$, as expected.

As a function of energy, the transmission coefficient rises from zero, fluctuates between maxima ($T = 1$) at $2k'a = n\pi$ and minima near $2k'a = (2n + 1)\pi/2$, and approaches the classical value $T = 1$ at the higher energies. Figures 6.9 and 6.10 show this behavior for two different values of $\beta = \sqrt{2\mu V_0 a^2}/\hbar$. The maxima occur when the distance $4a$ that a particle covers in traversing the well and back equals an integral number of de Broglie wavelengths, so that the incident wave and the wave which has been reflected inside the well are in phase reinforcing each other. If the well is deep and the energy E low (β and $\varepsilon' \gg 1$), the peaks stand out sharply between comparatively flat minima (see Figure 6.11). When the peaks in the transmission curve are pronounced, they are said to represent *resonances*. The energy values at which T reaches its maximum are determined by precisely the same condition as the truly discrete energy levels in an infinite square well of the same width [(6.90)].

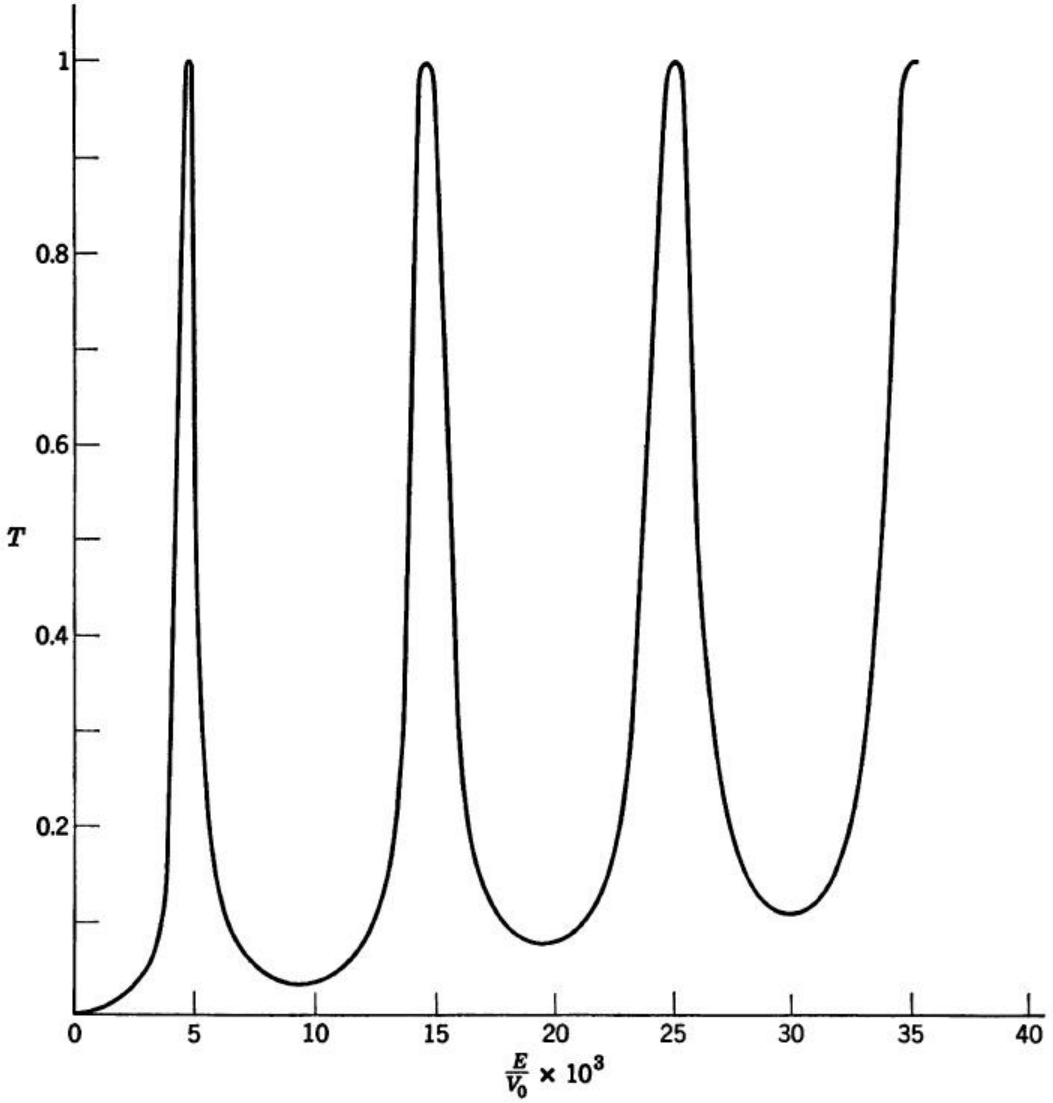


Figure 6.10. Transmission coefficient T versus E/V_0 for a square well with $\beta = 315$. As E increases, the resonances become broader.

It is instructive to consider the motion of a simple wave packet like (3.5) incident from the left upon the square well

$$\psi_{\text{inc}}(x, t) = \int_0^\infty f(k) e^{i(kx-\omega t)}\, dk \tag{6.94}$$

for $x < -a$. Hence $\omega = \hbar k^2/2\mu$, and $f(k)$ is assumed to be a real positive function with a peak at $k = k_0$ (>0), corresponding to a velocity v_0 and energy E_0. As was discussed at length in Chapter 2, the location of the peak of the wave packet $\psi(x, t)$ is determined by the requirement of stationary phase evaluated at $k = k_0$. Thus the peak (6.94) moves uniformly toward the right

according to the equation

$$x = \frac{\hbar k_0}{\mu} t = v_0 t \tag{6.95}$$

In the presence of a square well, (6.94) cannot be the complete wave function. For $x < -a$ there is also a reflected wave. If we set, with $G = 0$,

$$\frac{F}{A} = \frac{1}{M_{11}} = S_{12} = \sqrt{T}\, e^{-i\varphi} \tag{6.96}$$

$$\frac{B}{A} = \frac{M_{21}}{M_{11}} = S_{11} = \sqrt{1 - T}\, e^{-i(\varphi \pm \pi/2)} \tag{6.97}$$

thus defining a *phase shift* φ, the reflected wave may be written as

$$\psi_{\text{refl}}(x, t) = \int_0^\infty f(k)\sqrt{1 - T}\, e^{-i(kx + \omega t + \varphi \pm \pi/2)}\, dk \tag{6.98}$$

The peak of this wave packet is determined by

$$\frac{d}{dk_0}[k_0 x + \omega_0 t + \varphi(k_0)] = 0$$

which leads to the equation of motion

$$x = -v_0\left[t + \hbar\left(\frac{\partial \varphi}{\partial E}\right)_{k=k_0}\right] \tag{6.99}$$

for $x < -a$. The time delay between arrival of the incident wave peak and the appearance of the reflected peak at the left edge of the well is $2a/v_0 - \hbar(\partial\varphi/\partial E)$, and Figure 6.11 displays this time interval (dotted curve minus solid curve).

Finally, there is to the right of the square well ($x > a$) the transmitted wave packet:

$$\psi_{\text{trans}}(x, t) = \int_0^\infty f(k)\sqrt{T}\, e^{i(kx - \omega t - \varphi)}\, dk \tag{6.100}$$

The equation of motion of its peak is

$$x = v_0\left[t + \hbar\left(\frac{\partial \varphi}{\partial E}\right)_{k=k_0}\right] \tag{6.101}$$

for $x > a$.

The *phase shift* φ can be calculated from (6.91). We find

$$\varphi = 2ka - \arctan\left(\frac{\varepsilon'}{2}\tan 2k'a\right) \tag{6.102}$$

Exercise 6.14. Prove relation (6.102).

Figure 6.11 shows that the phase shifts also are subject to resonant behavior.

The interpretation of (6.101) is straightforward. If the potential well were absent, the coordinate of the center of the wave packet would be $x = v_0 t$ at all times, but since the particle moves faster inside the well than outside, it reaches the region $x > a$ earlier by an interval $\hbar(\partial\varphi/\partial E)$ than it would if V_0 were zero. If the well is deep and v_0 small, which is the condition for resonances to appear, this time interval would classically be approximately equal to $2a/v_0$ but $\hbar(\partial\varphi/\partial E)$ generally differs from the classical value. At the resonances it has the approximate value a/v_0, indicating that quantum mechanics introduces a time delay a/v_0 into the transmitted (and also the reflected) wave. This delay is a result of the wave nature of matter which causes repeated reflections back and forth in the well. Figure 6.12 gives us an idea of the number of times the wave packet bounces to and fro inside the well before it escapes. It should be noted that our estimate of the time delay introduced by the well is necessarily crude, since near resonance the shape of the wave

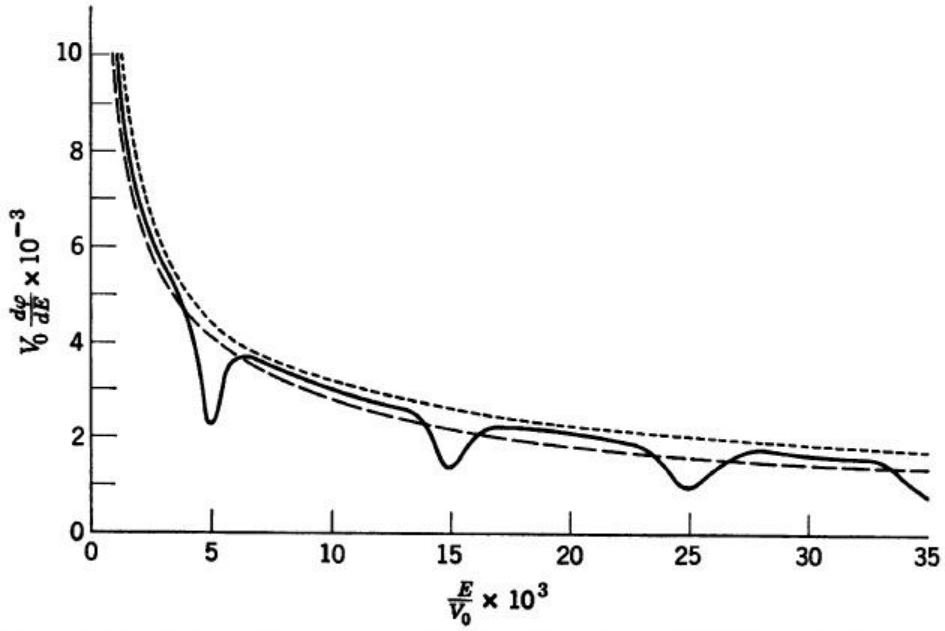


Figure 6.11. $V_0(d\varphi/dE)$ measures the time (in units of $\hbar/V_0$) by which a wave packet transmitted through a square well ($\beta = 315$) *precedes* a particle which, simultaneously released, moves with constant speed $v_0 = \sqrt{2E/\mu}$ throughout. The dashed curve corresponds to the advance of a classical particle moving through the well. The dotted curve is drawn for a classical particle assumed to move through the well with infinite speed. Since there can be no transmission before the incident particle has reached the well, the dotted curve is an upper limit for the time advance.

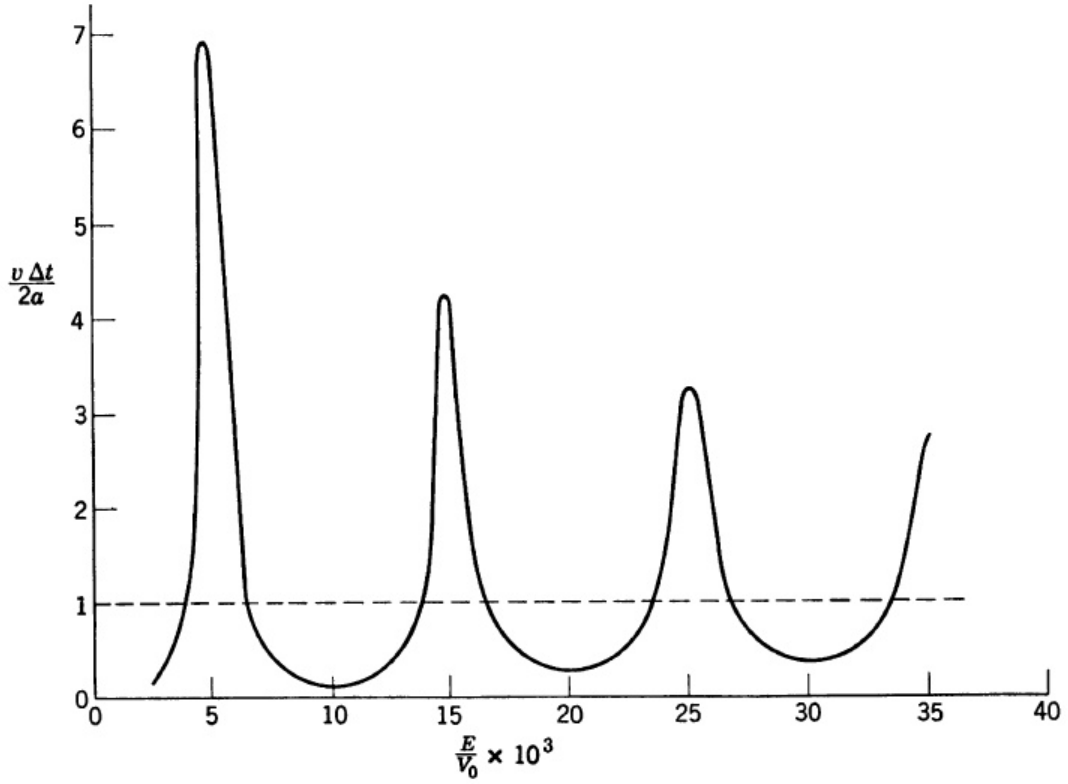


Figure 6.12. Average time Δt spent by a wave packet in the well ($\beta = 315$) in units of the time, $2a/v$, which it takes a particle of energy E to traverse the well. At higher energies the classical value, unity, is approached.

packet is drastically distorted and (6.101) represents an average position of the packet rather than the coordinate of its peak (see Section 7.4).

Exercise 6.15. Show that at a resonance of energy E_0,

$$\frac{\partial \varphi}{\partial E} = \frac{a}{\hbar v_0} \frac{1}{1 + (E_0/V_0)}$$

Resonance peaks in the transmission of particles are typical quantum features, and the classical picture is not capable of giving a simple account of such strong but smooth energy variations. Classically, depending on the available energy, T can only be zero or one, whereas in quantum mechanics T changes continuously between these limits.[10] Thus in a certain sense quantum mechanics attributes to matter more continuous and less abrupt characteristics than classical mechanics.

[10] The transmission coefficient for a potential barrier, Figure 6.5, is different from zero, although numerically small, for $E < V_0$ [(6.45)] and also varies continuously with energy. Classically, T jumps from 0 to 1 at $E = V_0$.

While these observations have general validity, it should be stressed that their verification by extending the solutions of the Schrödinger equation for discontinuous potentials to the classical limit meets with some obstacles.[11] For example, the reflection coefficient (6.38) is a function of the particle momentum only and, hence, it is apparently applicable to a particle moving under classical conditions. Yet classically, R is either 0 or 1. This paradox is resolved if we recognize that the correct classical limit of the quantum equations is obtained only if care is taken to keep the de Broglie wavelength short in comparison with the distance over which the fractional change of the potential is appreciable. The Schrödinger equation for the piecewise constant potential patently violates this requirement, but the next chapter will deal with potentials for which this condition is well satisfied.

Problems

1. Obtain the transmission coefficient for a rectangular potential barrier if the energy exceeds the height V_0 of the barrier. Plot the transmission coefficient as a function of E/V_0 (up to $E/V_0 = 3$) choosing $(2\mu V_0)^{1/2}a = 0.75h$.
2. Consider a potential $V = 0$ for $x > a$, $V = -V_0$ for $a \geqslant x \geqslant 0$, $V = +\infty$ for $x < 0$. Show that for $x > a$ the positive energy solutions of the Schrödinger equation have the form

$$e^{i(kx+2\delta)} - e^{-ikx}$$

   Calculate the *scattering coefficient* $|1 - e^{2i\delta}|^2$ and show that it exhibits maxima (resonances) at certain discrete energies if the potential is sufficiently deep and broad.
3. Solve the Schrödinger equation in one dimension for an attractive delta function potential by regarding it as an infinitely deep and narrow square well such that V_0a remains finite. Show that there is one bound state and calculate its energy. Verify the result by integrating the Schrödinger equation directly. Also calculate the transmission coefficient for positive energies.
4. A particle of mass μ moves in the one-dimensional double well potential

$$V(x) = -g\,\delta(x - a) - g\,\delta(x + a)$$

   If $g > 0$, obtain transcendental equations for the two energy eigenvalues of the system. Estimate the splitting between the energy levels in the limit of large a.

   If there is in addition a repulsive interaction $V = \lambda g/(2a)$ between the wells ("atoms"), show that, for a sufficiently small value of λ, the system ("molecule")

[11] For other interesting manifestations of abrupt changes in a potential, see the computer generated films on *Scattering in One Dimension*, Parts I to IV, produced by the MIT-Education Research Center and the Education Development Center, Newton, Mass. The fabrication of the films is described by their authors A. Goldberg, H. M. Schey, and J. L. Schwartz, *Am. J. Phys.*, **35**, 177 (1967). For information about these and other films on quantum mechanics, see W. R. Riley, Resource Letter BSPF-1, *Am. J. Phys.* **36**, 1 (1968).

is stable if the particle ("electron") is in the even parity state. Sketch the total potential energy of the system as a function of a.

If $g < 0$, calculate the transmission coefficient and show that it exhibits resonances.

5. In the periodic potential of Section 6.7 let the "hills" become delta functions by letting $a \to 0$ and $V_0 \to \infty$ such that $V_0 a$ remains finite. Show that the eigenvalue condition becomes

$$\cos \mathrm{k}l = \cos 2kb + (C/2kb) \sin 2kb$$

and make a graph of the function on the right-hand side versus $2kb$ for $C = 3\pi/2$. Exhibit the occurrence of allowed and forbidden energy bands.

6. Prove that $\mathrm{k}l = 2k'a + 2kb$ in the limit of high energies for the periodic potential of Section 6.7, and compare the numerical consequences of this relation with the exact curve in Figure 6.6.